



the Acid Deposition Research Program

BIOPHYSICAL RESEARCH

ENVIRONMENTAL SULPHUR ISOTOPE STUDIES IN ALBERTA: A REVIEW

by:

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February, 1987

PRIME RESEARCH CONTRACTOR:

The Kananaskis Centre for Environmental Research
The University of Calgary
Calgary, Alberta, Canada



88-00573/

The Acid Deposition Research Program is funded and administered by the Province of Alberta, the Canadian Petroleum Association, Alberta's electrical utilities and the Energy Resources Conservation Board.

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for submission to:

The Acid Deposition Research Program
1500, 633 Sixth Avenue S.W.
Calgary, Alberta, Canada T2P 2Y5

February 1987

This publication may be cited as:

Krouse, H.R. 1987. **Environmental Sulphur Isotope Studies In Alberta: A Review.** Prep for the Acid Deposition Research Program by The Department of Physics, The University of Calgary, Calgary, Alberta, Canada. **ADRP-B-03-87.**
89 pp.

ISBN 0-921625-05-7 (Volume 3)

ISBN 0-921625-02-2 (Set of 11)

EXECUTIVE SUMMARY

Environmental sulphur isotope studies have been conducted in Alberta since the late 1960's. To date, thousands of analyses have been carried out for sulphur compounds or extracts from the atmosphere, hydrosphere, pedosphere, and biosphere. From the viewpoint of using stable isotopes to trace pollutant sulphur (S) in the environment, Alberta is among the few places in the world where industrial emissions differ greatly in isotopic composition from those of the preindustrial environments. Consequently, these investigations have not only served to identify and trace industrial S at locations in Alberta, but have contributed immensely to our understanding of fundamental concepts concerning uptake and utilization of sulphur by environmental acceptors.

Many instances have been cited where stable isotope investigations have saved many times their costs by avoiding expensive mistakes. This is particularly true for the mineral and fossil fuel industries where, on the basis of isotope data, money was not wasted in further non-rewarding exploration. The important point in environmental studies is that stable isotope abundances can usually provide information on the source of pollutants. Very few techniques have this capability; examples of techniques that do include high resolution mass spectrometry and neutron activation analysis of trace molecules in air samples. Conventional concentration measurements fail to apportion sources. Cases can be cited where high concentrations of sulphate have been wrongly attributed to an industrial source. Therefore, concentration measurements should be accompanied by sufficient isotope abundance determinations.

Basic principles of stable isotopes which pertain to sulphur pollution include the following:

1. Isotopes of an element differ in their masses. Since many processes are mass dependent, the relative abundances (the ratio of the number of ^{34}S atoms to ^{32}S atoms) in natural components are altered.
2. The process which alters sulphur isotope abundances most significantly is bacterial SO_4^{2-} reduction during which $^{32}\text{SO}_4^{2-}$ is converted faster than $^{34}\text{SO}_4^{2-}$ to sulphide.
3. Because of the above, pollutants usually differ in isotopic composition from their environmental receptors.
4. On the basis of (3), the presence of pollutant sulphur in the environment, and often the ratio of pollutant-to-natural sulphur, may be determined.
5. Successful isotope tracing of pollutant sulphur requires minimal isotope fractionation during transport and deposition. This criterion is difficult to meet in anaerobic environments because of (2) above. However, most studies of the atmosphere, water, and soil involve aerobic conditions where the following processes have minimal isotopic selectivity:
 - a. Chemical or bacterial oxidation; addition of oxygen does not greatly influence the sulphur isotope composition.
 - b. High temperature processes, e.g., in power plant stacks. Isotope fractionation decreases with increasing temperature.

- c. SO_4^{2-} assimilation by bacteria or plants.
 - d. Reactions of sulphur compounds in the solid state, such as dissolution of evaporites or oxidation of elemental sulphur. The reaction proceeds essentially layer by layer thus limiting isotopic selectivity.
 - e. Conversions among larger complex molecules if bond rupture involves large fragments of the molecule. In that case, isotopic substitution does not produce a large percent mass change in the species undergoing reaction.
6. An exception to (5) is the isotopically selective emission of reduced sulphur compounds by vegetation under stress. Therefore, enrichment of heavier sulphur isotopes in vegetation above that for known sources can serve as a stress indicator.
 7. Since the uniform isotope composition of O_2 in the atmosphere differs greatly from the variable isotopic composition of water, oxygen isotope measurements on sulphate provide information concerning the oxidation of pollutant sulphur.
 8. Isotopic data should be considered as a complementary rather than an alternate tool. With the exception of (6), isotope data per se do not relate environmental damage to source. They must be used in combination with biological data.
 9. Isotope data are most effective when background measurements are taken prior to commencement of an industrial operation. This is seldom the case. However, it is often possible to estimate the background conditions. Further, it is useful at any time to establish an isotopic "baseline" with which future measurements might be compared.

Further isotopic data may identify an important phenomenon which is not discernible from conventional concentration data. For example, unusual enrichments of the heavier ^{34}S in foliar S are consistent with isotopically selective emissions of reduced S under environmental stress. The concentrations of S in foliage would not provide evidence of this biochemical reaction.

The studies in Alberta have been on the leading edge of the global investigations of anthropogenic S in the environment. Material from these studies has been the subject of significant chapters in two books: Handbook of Environmental Isotope Geochemistry, Vol. 1. The Terrestrial Environment, eds. P. Fritz and J.Ch. Fontes (1980), and the American Society of Agronomy Monograph Sulphur in Agriculture, ed. M.A. Tabatabai (1986).

A review of the studies in Alberta per se is long past due. Attempts to do so in the past have been perturbed by the desire of agencies for more data and the requests to communicate fundamental findings to the international community. This particular review has the feature that many data are appearing in the public domain for the first time.

Developments which set the stage for applying sulphur isotopes to environmental studies in Alberta are listed below. It must be realized that developments seldom resulted solely within one project but rather evolved from the accumulated data of

several projects over the years. Further, the time between discoveries and publication in open journals varied depending upon the circumstances. The list below is, therefore, not strictly chronological. The accompanying map shows some of the locations in Alberta where stable sulphur isotope investigations have been carried out.

1. Hydrogen sulphide evolved to the atmosphere from springs in the Rocky Mountains of Alberta is depleted in the heavier sulphur isotopes as the consequence of bacterial SO_4^{2-} reduction (Krouse et al. 1970).
2. The first study of sulphur isotope abundances in soils revealed $\delta^{34}\text{S}$ values* near 0‰ in central Alberta and as low as -30‰ in the Peace River area (Lowe et al. 1971). $\delta^{34}\text{S}$ values near 0‰ have since been found for soils in many locations, e.g., Ram River (Krouse 1977b) and West Whitecourt study area (Krouse et al. 1984). Very negative values have been found at Teepee Creek (Krouse and Case 1981) and near small lakes in the Twin Butte area (Section 5).
3. Dissolved sulphate in the Mackenzie River system was found to vary in sulphur isotope composition over almost the total range encountered globally for fresh water. Rivers draining the Peace River area have SO_4^{2-} with highly negative $\delta^{34}\text{S}$ values consistent with soils data for that region (Hitchon and Krouse 1972).
4. In contrast to the above, sour gas (H_2S -rich) in carbonate reservoirs of Alberta has quite positive $\delta^{34}\text{S}$ values (Krouse 1977a).
5. Consistent with statement 4, the air in Alberta near sour gas plant operations tends to have SO_2 enriched in ^{34}S (i.e., positive $\delta^{34}\text{S}$ values) in comparison to the global average.
6. Ground level SO_2 near Crossfield, Alberta became more enriched in ^{34}S as the sour gas processing plant went from shutdown to full production. The $\delta^{34}\text{S}$ value ($+29\text{‰}$) of the stack gas was mathematically predicted from the ground level data and experimentally verified using a helicopter mounted high volume sampler (Krouse 1980).
7. Effects of wind direction on the isotopic composition of SO_2 reaching a monitoring site were documented in the West Whitecourt Case Study (Krouse et al. 1984). A wind-direction activated array of high volume samplers was tested.
8. The presence of sulphur of industrial origin was documented isotopically in surface waters near sour gas processing plants, e.g., Valleyview (Krouse and Case 1983) and the West Whitecourt study area (Krouse et al. 1984).
9. A correlation was found between the sulphur isotope composition of SO_4^{2-} and the dissolved organic S content in surface waters in the West Whitecourt case study, indicating that industrial S interacted with organic matter in the environment (Krouse et al. 1984).

* The $\delta^{34}\text{S}$ scale is defined in Section 1.1.



10. In the Calgary river system, lateral mixing of SO_4^{2-} is slow. Hence, different sources of effluents might be identified by a cross-sectional isotopic study (Krouse 1980).
11. Random sampling in the Ram River area over two years showed that epiphytic lichens had a $\delta^{34}\text{S}$ distribution similar to atmospheric SO_2 (Krouse 1977b).
12. Lichens in the Fox Creek area had higher $\delta^{34}\text{S}$ values in locations more exposed to SO_2 emissions; those on the lee side of hills had lower values than those exposed on the windward side (Case and Krouse 1980).
13. In contrast to statement 11, conifer needles had $\delta^{34}\text{S}$ values intermediate to those of atmospheric SO_2 and the soil. This demonstrated that foliage could acquire sulphur from the atmosphere as well as by transportation from the root system (Krouse 1977b). This phenomenon has been verified in the several referenced field studies.
14. Foliar uptake of sulphur from the atmosphere and soil was further demonstrated isotopically in the field with potted plant experiments (Winner et al. 1978).
15. The sulphur isotopic composition of mosses was found to vary with downwind distance and direction near a sour gas plant operation in the Fox Creek area. Higher $\delta^{34}\text{S}$ values corresponded to closer proximity to the source of emissions (Winner et al. 1978).
16. Ground lichens and mosses tend not to be as enriched in ^{34}S as those on trees in the same area, e.g., Brazeau (Latonas et al. 1986).
17. Moss was found capable of trapping atmospheric S compounds, thus preventing their transport to the subsoil (Krouse 1980). Litter generally is capable of blocking the downward movement of wet and dry fallout of S-compounds (Legge et al. 1986).
18. Conifer needles may display more positive $\delta^{34}\text{S}$ values with increasing height on a given tree (unpublished data, Ram River 1972; Krouse et al. 1984). This can be explained by upper foliage exerting a canopy action to shield underlying foliage from atmospheric S compounds (Lester et al. 1986).
19. Consistent with statement 18, the uppermost needles of lodgepole pine were found to be unusually enriched in ^{34}S compared with those lower in the canopy (Krouse et al. 1984).
20. Some lichens in the Fox Creek area had unusually high $\delta^{34}\text{S}$ values, suggesting that under sulphur stress, gaseous compounds depleted in $\delta^{34}\text{S}$ were emitted (Case and Krouse 1980).
21. Laboratory experiments showed that H_2S was emitted by cucumber plants grown with roots in high concentrations of SO_4^{2-} and HSO_3^- . The H_2S was depleted in ^{34}S by as much as 15‰ as compared to the nutrient solutions (Winner et al. 1981).

22. In the Teepee Creek area of Alberta, sulphur isotope data revealed that foliage and soils with high sulphur contents are associated with shallow subsurface sulphate mineral deposits. These natural sulphur sources, quite depleted in ^{34}S , dominated the environmental sulphur cycle in that area (Krouse and Case 1981).
23. Sulphur isotope analyses of soil cores near Valleyview, Alberta were used to document penetration of sulphur of industrial origin into the subsoil in the vicinity of a flare stack which had been operational for over two decades (Krouse and Case 1983). The most comprehensive data attesting to vertical subsoil movement of sulphur of industrial origin has been obtained in the West Whitecourt study area (Legge et al. 1986).
24. With respect to statement 22, soil texture was found to be an important factor with clay particles retaining S-compounds to a greater extent than sand (Krouse and Case 1983).
25. Other factors influencing the penetration of industrial S into the subsoil are vegetative cover (Statement 17), duration of emissions, and hydrology (Krouse et al. 1984).
26. In soil profile studies, isotope data revealed that sampling by horizon is more meaningful than sampling pre-selected depth intervals.
27. Sulphur isotope data from the Zama area and elsewhere strongly suggest that in rolling terrain, sulphate minerals accumulating in depressions may contribute to visible stress symptoms, whereas plants on knolls may be growing in S-deficient soil. The latter may display the isotopic signature of industrial emissions and may actually be thriving on atmospheric sulphur (Krouse and Case 1982).
28. As sulphur is passed up the food chain, the isotopic discrimination is minimal, i.e., animals have a sulphur isotope composition similar to their diets. Citizens of Calgary were found to have remarkably consistent $\delta^{34}\text{S}$ values (near 0‰) in their hair, nails, blood, kidney stones, and urine.

Despite the many thousands of analyses, more data are required in several areas. These include:

1. Studies of lake sediments over small depth increments to see if a time marker is registered by an isotopic signature attributable to industrial processing. This should permit comparison of pre-industrial and current fluxes of S to lakes and ponds.
2. Data are generally sparse for surface waters and groundwater. The source of SO_4^{2-} in groundwaters in alkali soil areas could prove of value for future agricultural practices. It has been argued that lakes in Alberta are well buffered to deal with acidic precipitation and runoff. Isotopic analyses should show just how well lakes in affected areas are coping.

3. Oxygen isotope data on sulphate in wet- and dryfall are virtually non-existent. Comparison of oxygen isotope data of water and sulphate may potentially delineate sulphate produced from atmospheric gaseous emissions and that from the oxidation of S^0 dust.
4. More data on insects and small mammals should be acquired to document migration of sulphur of industrial origin up the food chain.
5. Sulphur oxide emitting industrial installations should be encouraged to obtain sulphur isotope data for environmental receptors prior to commencing operations. If this has not been done, it is still useful to have reference values to which future data may be compared. An isotopic survey every five years or so is desirable.
6. Data acquisition has been biased in terms of sites surrounding sour gas plant installations. In terms of long range transport and studies of other emissions, e.g., coal-fired power plants, a more uniform sulphur isotope base should be established throughout the Province.

The time has also arrived when a sulphur isotope computer data base should be established for the Province of Alberta. In this way, the isotopic data could be better related to region, surface geology, natural and anthropogenic emissions, and so forth.

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ACKNOWLEDGEMENTS

A few years ago, the author was given leave from teaching duties for one term through support from The University of Calgary Killam Resident Fellowship Program to work on a book entitled "Sulphur Isotope Abundances in Subsurface and Surface Environments of Alberta." The similar opportunity provided by the Acid Deposition Research Program for this review has been complementary. The "subsurface" was emphasized during the Killam award whereas the "surface" has been examined in this report.

Initial sulphur isotope measurements of atmospheric sulphur compounds were carried out for samples supplied by S. Dobko of Alberta Environment in 1970. The first isotopic investigation of vegetation was carried out in the Ram River area with financial assistance from Aquitaine Ltd. This work demonstrated that foliar sulphur was derived from both the air and soil. Further studies on vegetation were supported by the Canadian Forestry Service.

Through a National Research Council Negotiated Development Grant, The University of Calgary Interdisciplinary Sulphur Research Group (UNISUL) was established in 1975 and the methodology further developed. The program was concurrently further enhanced by the effective interaction with Dr. A. Legge and other colleagues of the West Whitecourt Study Group.

In recent years, major investigations have been funded by Alberta Environment, where among others, Dr. H.S. Sandhu and Mr. A. Schulz have taken a keen interest in individual projects. Smaller projects were funded by resource companies including Chieftain, Dome Petroleum, Gulf, Hudson's Bay Oil and Gas, Petro Canada, and Esso Resources. G. Latonas, on behalf of Western Research Division of Bow Valley Resource Services Ltd., has been instrumental in initiating collaborative projects with industry.

Thus, Federal and Provincial agencies and the private sector have financially supported these studies. The success has also depended in no small way upon interactions with many colleagues in industrial, government, and University laboratories.

A special thanks goes to the Acid Deposition Research Program for the funding to carry out this literature review.

Special acknowledgements also go to Allan Legge and Julie Lockhart for their assistance in the preparation and editing of this manuscript.

1. PRINCIPLES OF STABLE ISOTOPE RESEARCH

1.1 δ -SCALES

In stable isotope research, δ -scales are used to express isotopic abundances. The isotopic composition of a sample is usually expressed on a $\delta^{34}\text{S}$ scale, defined as:

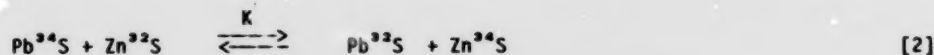
$$\delta^{34}\text{S in } \text{‰} = \left\{ \frac{[^{34}\text{S}/^{32}\text{S}] \text{ sample}}{[^{34}\text{S}/^{32}\text{S}] \text{ standard}} - 1 \right\} \times 10^3 \quad [1]$$

where ‰ (per mil) is parts per thousand, and $[^{34}\text{S}/^{32}\text{S}]$ is the ratio of the number of ^{34}S to the number of ^{32}S atoms in the sample or the standard. The standard used internationally is troilite (FeS) from the Canon Diablo meteorite. This relative scale has the distinct advantage that isotopic discriminations during measurement appear in both the numerator and denominator of equation [1] and, therefore, cancel. Consequently, $\delta^{34}\text{S}$ determinations can be made with a reproducibility of better than $\pm 0.1\text{‰}$ (1 part in 10,000). Positive and negative $\delta^{34}\text{S}$ values mean that the sample is "enriched" and "depleted" in ^{34}S , respectively, in comparison to the standard. Since a sample with a higher $\delta^{34}\text{S}$ value has a higher density, the jargon of the field includes the terms "heavy" and "light" in reference to positive and negative $\delta^{34}\text{S}$ values.

1.2 STABLE ISOTOPE FRACTIONATION

The altering of isotope abundances is termed "isotope fractionation" and is accomplished by exchange reactions and unidirectional processes. The fundamental concept underlying isotope fractionation is that isotopes of an element differ in their mass. This property may express itself simply in physical processes such as diffusion, where the diffusion coefficient is proportional to $(\text{mass})^{-1/2}$ of the diffusing species. In contrast, more complex functions of mass are associated with the different vibrational and rotational frequencies associated with isotopically distinguishable molecules.

Exchange of isotopes may occur between two different chemical species or between two phases of the same chemical compound. An example of the former is the exchange of S isotopes between galena and sphalerite;

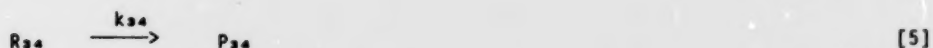
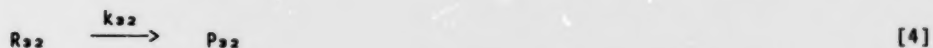


If equilibrium is realized, the isotopic equilibrium constant K is given by:

$$K = \frac{[^{34}\text{S}/^{32}\text{S}]_{\text{PbS}}}{[^{34}\text{S}/^{32}\text{S}]_{\text{ZnS}}} \quad [3]$$

Because the temperature dependence of the equilibrium constant is usually given by $\ln K \propto T^{-2}$ (Urey 1947; Bigeleisen and Mayer 1947), the isotopic compositions of natural co-existent minerals or phases can serve as a geothermometer if equilibrium exchange conditions have been realized.

Unidirectional processes giving rise to isotope fractionation include physical processes such as diffusion and evaporation as well as chemical processes wherein bonds are ruptured and constituted. These processes have the common feature that their isotopic rate constants differ. The isotopic competition in a simple one-step reaction may be written as follows:



where R and P are reactants and products, respectively, containing ^{32}S and ^{34}S as designated by the superscript. In the physical process of evaporation, R would be the liquid phase and P the vapour phase. The ratio of the isotopic rate constants k_{32}/k_{34} , also called the "kinetic fractionation factor", is usually >1 . In the case of a physical process such as diffusion, the lighter isotope moves faster. In chemical reactions, the lighter isotopic bonds vibrate at higher frequencies and are more readily broken.

The isotopic fractionation realized in exchange processes is determined by the value of the equilibrium exchange constant K and the extent to which equilibrium is approached. The isotopic fractionation achieved in unidirectional processes depends on the k_{32}/k_{34} values for the various steps, the relative rates of these steps, the extent of reaction, and the components of the reaction being examined. The isotopic behaviour of reaction components as a function of the extent of reaction for a one-step first order process is illustrated in Figure 1. The product forming at any time is depleted in ^{34}S with respect to the reactant. Hence, the remaining reactant becomes enriched in ^{34}S as the reaction proceeds. This is termed the "reservoir effect." The product formed at any instant has a $\delta^{34}\text{S}$ value approximately $[(k_{32}/k_{34})-1] \times 10^3$ less than that of the remaining reactant. On the other hand, the product accumulated to any point in the reaction can never have a $\delta^{34}\text{S}$ value greater than the initial reactant and acquires that isotopic composition at 100% conversion; i.e., all of the isotopes initially present in the reactant are in the product if the reaction goes to completion.

For many reasons, the simple model of Figure 1 seldom describes natural phenomena. It must be determined whether the instantaneous or the accumulated product curve applies. The former is appropriate if the product has precipitated as undisturbed layers. On the other hand, the latter fits situations where the product is well mixed; e.g., gases or ions in solution. In addition, many reservoirs in nature "leak" and may have numerous inputs and outputs. As an example, during microbiological reduction of SO_4^{2-} , sulphide may remain as HS^- in solution, precipitate as metal sulphides, or escape to the atmosphere as H_2S . Whereas the isotopic composition of any of these products should lie between the instantaneous and accumulated product curves of Figure 1, there is the distinct problem of accounting for all sulphide produced in order to calculate the percentage reaction.

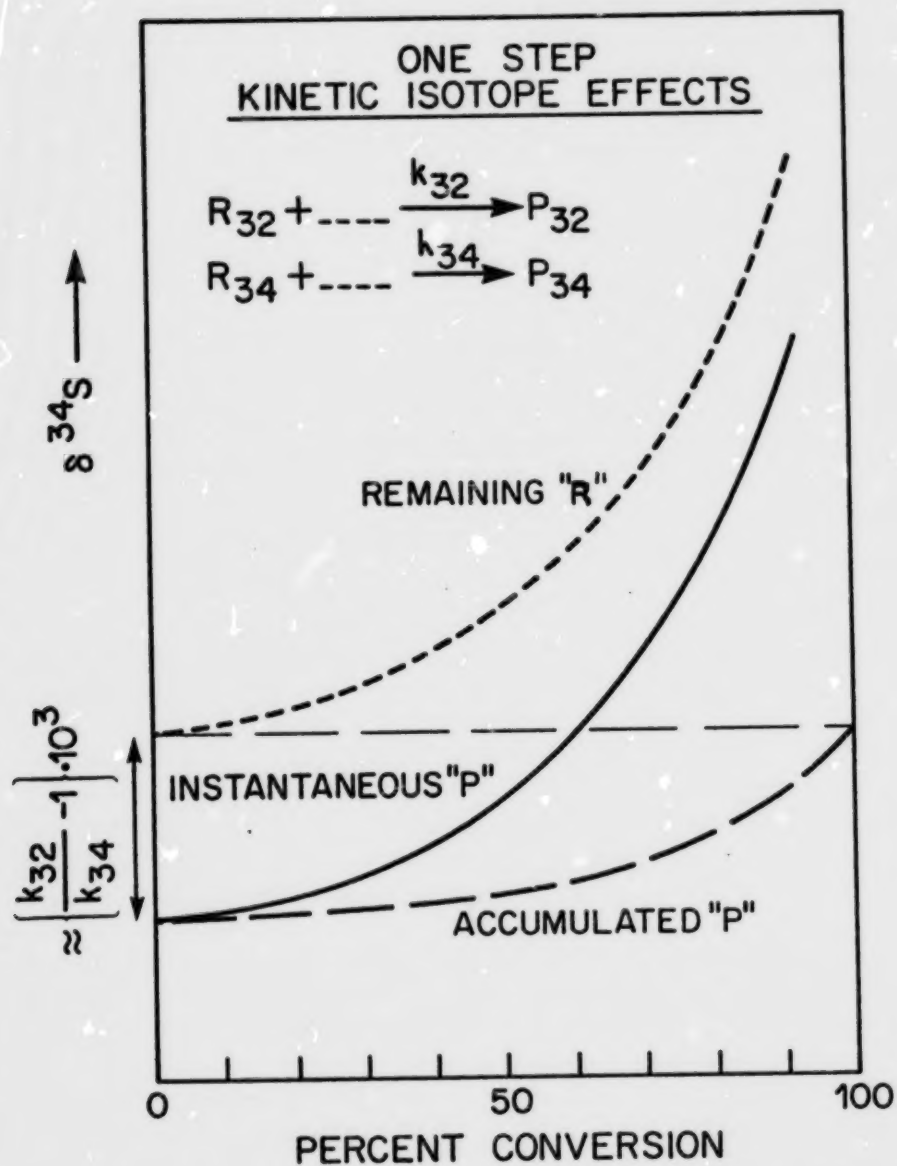


Figure 1. Isotopic behaviour of reaction components as a function of the extent of reaction for a one-step first order process.

1.3 THE USE OF STABLE ISOTOPES AS TRACERS

Stable isotopes serve as tracers in many ways. From the discussion above, it is realized that natural isotopic fractionation itself is indicative of the history of sulphur in a given specimen. If one is interested in delineating sources of sulphur be they natural, industrial, or experimentally introduced, plots of $\delta^{34}\text{S}$ versus various functions of concentration can prove useful. Several hypothetical models were discussed by Krouse (1980). In the case of two sources, isotopic balance is given by the approximate expression,

$$C\delta = C_A\delta_A + C_B\delta_B \quad [6]$$

where C and δ are the measured S concentration and $\delta^{34}\text{S}$ value in the samples. $C = C_A + C_B$ where C_A and C_B are the concentrations resulting from sources A and B, these sources having $\delta^{34}\text{S}$ values of δ_A and δ_B , respectively.

Substitution for C_B in equation [6] and rearrangement gives:

$$\delta = \frac{C_A(\delta_A - \delta_B)}{C} + \delta_B \quad [7]$$

This equation is general and pertains to gases, ions, fine particulates, or minerals which were once molten or in solution, the only assumption being thorough mixing in the volume of the fluid phase under consideration. In some cases, the equation applies to sulphur acquired by soil, plants, and animals (Section 4).

If the samples in the system being studied do not have a range of δ and C values, then information about sources A and B cannot be deduced. However, C_A or C_B usually vary, yielding different values for the measurable quantities δ and C . Equation [7] suggests that plotting $\delta^{34}\text{S}$ against the inverse of concentration may prove informative. If the data plot on a straight line, then the slope $C_A(\delta_A - \delta_B)$ and δ_B are constants. This in turn implies that δ_A and C_A are also constants. This is the case of one source A with isotopic composition δ_A contributing a constant C_A throughout the system and source B with isotopic composition δ_B contributing C_B values which are not uniform with respect to location and/or time. The y-intercept of the plot of δ versus inverse concentration is δ_B (Figure 2b).

For natural systems, only an upper limit for C_A and the corresponding δ can be obtained if there is no independent evidence that a data point corresponding to C_A and δ_A has been obtained. This situation is illustrated in Figure 2. An example of this case would be SO_2 emissions from an industrial stack with isotopic composition δ_B falling on level terrain with uniform soil having pre-industrial values C_A and δ_A . C_B would vary with location and time because of changing wind direction and rates of emission. C_A and δ_A may be known only if measurements were made prior to the start of the industrial operation. If measurements commenced well after the onset of emissions, then only an upper limit for C_A can be obtained. One might measure at greater distances from the stack hoping to obtain a better value for C_A . In doing so, there are the uncertainties that either another source may influence those locations or the pre-industrial C_A and δ_A values were not consistent over those distances.

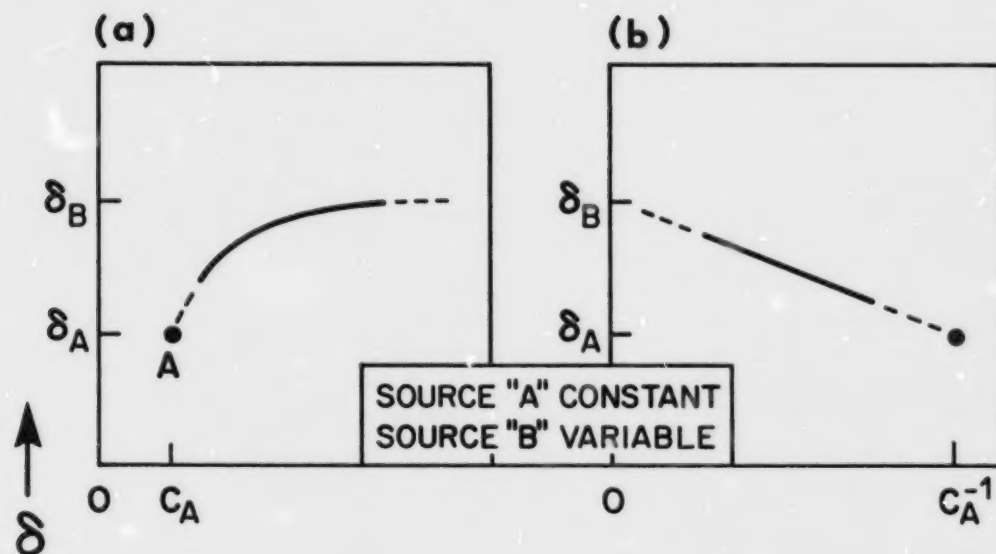


Figure 2. Plot of $\delta^{34}\text{S}$ versus concentration (a) and concentration $^{-1}$ (b) for mixtures of sulphur from two sources. Source A has a constant emission rate and isotopic composition δ_A . Source B has a different constant isotopic composition δ_B but varies in its emission rate.

If data of the $\delta^{34}\text{S}$ versus inverse concentration plot fall into an area which can be extrapolated to form a triangle, then the situation is that described above plus an additional source C with isotopic composition C and contributing variable C_C to the system. Such a case is illustrated for soil in the Twin Butte area of Alberta.

2. SULPHUR ISOTOPE ABUNDANCE VARIATIONS IN NATURE

2.1 GENERAL DISTRIBUTION OF SULPHUR ISOTOPES

Massive reservoirs of S exist on Earth, such as oceanic and evaporitic SO_4^{2-} , organic S compounds in shales, and more localized smaller occurrences such as sulphide ore deposits and geothermal and volcanic emanations. All of these reservoirs contribute S to soils and plants by either natural or industrial processes. A small industrial operation may change significantly the concentrations and isotopic composition of S compounds in the pedosphere, hydrosphere, and atmosphere. For these reasons, satisfactory interpretation of the $\delta^{34}\text{S}$ values currently found in soils and plants requires a knowledge of the overall geochemistry of sulphur isotopes.

The initial study of Thode et al. (1949) revealed large variations in the isotopic composition of S compounds in nature. Sulphur has proved to be an interesting element to study in this regard because it exists in many forms and valence states, and numerous terrestrial processes alter its isotope composition. A summary of the variations in $\delta^{34}\text{S}$ values is given by Figure 3. The choice of meteoritic troilite (FeS) as an international standard is excellent because of its consistency in isotopic composition and its proximity to the mean of the terrestrial range.

As predicted from statistical thermodynamics, there is a tendency for ^{34}S enrichment in the higher valence state compounds such as SO_4^{2-} where more S-containing bonds are involved, whereas ^{34}S depletions are usually found in reduced forms of S. The S cycle, however, is far from isotopic equilibrium and unidirectional processes tend to promote the wide variations in $\delta^{34}\text{S}$ values.

A few samples fall well outside of the range shown in Figure 3. Barite concretions may have $\delta^{34}\text{S}$ values as high as +90 (Sakai 1971; Shakur 1982). $\delta^{34}\text{S}$ values as low as -45 have been found in hydrotroilite (Veselovsky et al. 1969) and pyrite in cores from the Deep Sea Drilling Project (DSDP) leg 37 (Krouse et al. 1977). A range from -47 to +70 has been reported for $\delta^{34}\text{S}$ in pyrite concentrations in one study (Bogdanov et al. 1971).

2.2 MICROBIOLOGICAL SULPHUR ISOTOPE FRACTIONATION

It is seen in Figure 3 that materials which range widely in their sulphur isotope composition are also those which have possibly participated in redox reactions in the bacterial S cycle. A number of review articles summarize hundreds of laboratory experiments designed to study microbiological fractionation of S isotopes (Krouse and McCready 1979a, 1979b; Chambers and Trudinger 1979; and Krouse 1980).

Direct primary production of organically bound S results during assimilatory reduction of SO_4^{2-} by living plants and microorganisms. During the process, organic S compounds are synthesized and retained in cell structures. It has often been stated that the isotope fractionation during this process is negligible because the organic S is usually depleted in ^{34}S from between 0 to 4‰ relative to dissolved SO_4^{2-} . This is found for a variety of microorganisms and plants. Much larger depletions in ^{34}S have been realized with the yeast Saccharomyces cerevisiae grown on pantothenate-deficient media (McCready et al. 1974, 1979).

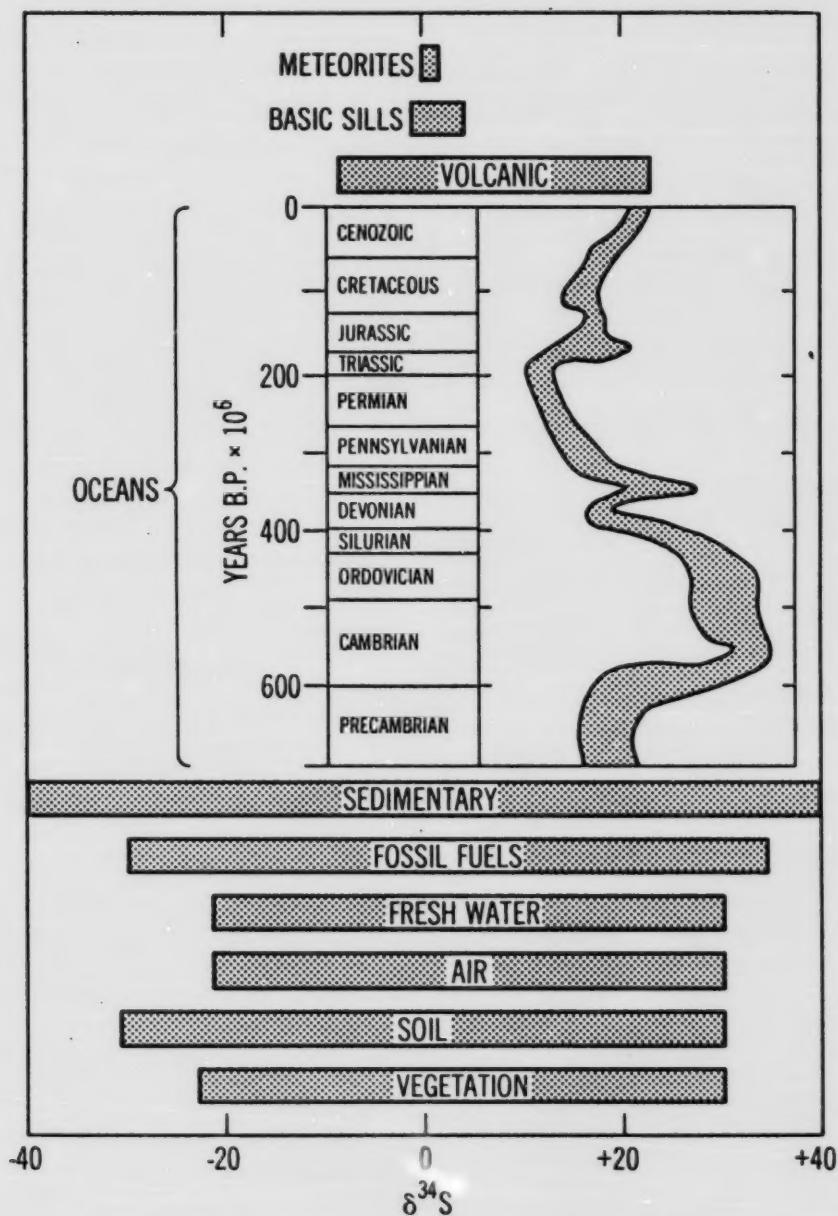


Figure 3. Sulphur isotope variations in nature (taken from Krouse and Tabatabai 1986; oceanic curve is after Claypool et al. 1980).

During chemosynthetic or respiratory oxidation by Thiobacillus, sulphide can be oxidized to S^0 , polythionates, and SO_4^{2-} . Using growing cells of Thiobacillus concretivorus, Kaplan and Rittenberg (1964) found $\delta^{34}S$ values of these products to be -0 , $+1$ to $+19$, and -10 to -18 , respectively, with respect to starting sulphide. With photosynthetic bacterial oxidation, the results are conflicting for different microorganisms. It should be noted that a Na_2S solution in sunlight will oxidize to SO_4^{2-} which is -6‰ compared with the starting sulphide (Krouse, unpublished data), and this purely chemical oxidation may influence bacterial studies.

Sulphate produced from bacterial oxidation of elemental S is not significantly different isotopically from the S^0 . This has been verified with many isolated species, mixed cultures, and field experiments (c.f. McCready and Krouse 1982). The lack of isotopic selectivity probably relates to the solid phase of the reactant which should be oxidized successively layer by layer.

Dissimilatory SO_4^{2-} reduction by the classical anaerobes Desulphovibrio and Desulphotomaculum in laboratory experiments has generated H_2S ranging in $\delta^{34}S$ from $+3$ to -46‰ as compared with the initial SO_4^{2-} . Qualitatively, the degree of fractionation is an inverse function of the reduction rate per unit cell. However, at any rate, the range is substantial and increases in going to lower rates. Harrison and Thode (1958) explained instantaneous depletions of ^{34}S in the evolved H_2S (0 to -25‰) by a two-step mechanism. Values near zero corresponded to a step with negligible isotopic discrimination, competing for rate control, whereas values near -25‰ corresponded to $S-O$ bond rupture controlling the overall reaction rate. This model does not describe the greater depletions such as -46‰ realized with D. desulfuricans using ethanol as a carbon source (Kaplan and Rittenberg 1964).

Rees (1973) developed a steady state model of bacterial SO_4^{2-} reduction which included external SO_4^{2-} , internal SO_4^{2-} , APS (adenylyl sulphate), sulphite, and H_2S in the reaction scheme. He assigned an inverse isotope effect of $+3\text{‰}$ for SO_4^{2-} uptake, and -25‰ for initial $S-O$ ruptures of SO_4^{2-} and SO_3^{2-} . His model also permits zero-order kinetics for SO_4^{2-} uptake at higher SO_4^{2-} concentrations. Such a model can account for all the data from laboratory SO_4^{2-} reduction experiments and field observations.

In nature, there is no doubt that the SO_4^{2-} -reducing bacteria are producing isotopically light sulphide, and further, these depletions often exceed those found in laboratory experiments. Sulphur isotope data for a number of springs around the world have been summarized by Krouse (1976). In a regional study in the Northwest Territories of Canada, the apparent k_{32}/k_{34} values often exceeded 1.06 (Weyer et al. 1979). Unreacted SO_4^{2-} in ice-covered stratified lakes on Ellesmere Island has $\delta^{34}S$ values exceeding $+100\text{‰}$ because of bacterial reduction and the reservoir effect depicted in Figure 1 (Jeffries et al. 1984). Although large fractionations are not usually consistent with nutrient-rich environments, values of -55‰ were found for HS^- in an ice covered sewage treatment lagoon for the City of Camrose, Alberta (Krouse 1980). Presumably, the low temperatures realized slow conversion rates per unit cell and this was accompanied by large fractionation as found in laboratory experiments.

There are also many examples in nature in which the isotopic evidence attests to very little fractionation during oxidation of sulphide. In fact, elemental sulphur is apparently not an intermediate during reduction processes and must form during

sulphide oxidation. Thus, S^0 found associated with springs in western Canada tends to have a $\delta^{34}S$ value near that of HS^- in the surrounding water, which is in turn significantly depleted in $\delta^{34}S$ compared with the SO_4^{2-} (Krouse et al. 1970).

2.3 SULPHUR ISOTOPE ABUNDANCES IN THE LITHOSPHERE

Soil originates by complex mechanisms in the weathering of rocks and mixing with partly decomposed plant and animal debris. Any type of rock -- igneous, sedimentary, or metamorphic -- may provide the parent material for a soil. Hence, a brief overview of sulphur isotope abundances in the lithosphere is appropriate.

Deep seated primary sulphides tend to have $\delta^{34}S$ values near the meteoritic troilite reference as revealed by studies of basic sills (Shima et al. 1963; Smitheringale and Jensen 1963), igneous sulphides (Thode et al. 1962; Ryznar et al. 1967; Schneider 1970; and Schwarz 1973), and carbonatites (Grinenko et al. 1970; Mitchell and Krouse 1975). Some volcanogenic deposits have $\delta^{34}S$ values removed from 0 because of isotope exchange processes and/or because sources of S are other than primary minerals (Rafter and Wilson 1963).

Sedimentary sulphides show a much greater spread in $\delta^{34}S$ values and perhaps a tendency to be depleted in the heavier ^{34}S . This can be attributed in some instances to kinetic isotope effects during bacterial reduction. However, Ohmoto (1972) demonstrated that in ore-forming fluids, shifts in chemical equilibria among aqueous species coupled with exchange reactions could deplete sulphides in ^{34}S by 20‰ even at temperatures exceeding 250°C. In some cases, sedimentary stratabound sulphide deposits have quite positive $\delta^{34}S$ values, indicating derivation from ancient seawater sulphate with modest isotope fractionation (Campbell et al. 1968; Sasaki and Krouse 1969).

Marine evaporite sulphates are enriched in ^{34}S , ranging from <+10‰ to >+35‰. The variations attest to amazing temporal variations in the isotopic composition of ancient oceanic sulphate (Nielsen and Rieke 1964; Thode and Monster 1965; Holser and Kaplan 1966; Davies and Krouse 1975; and Claypool et al. 1980). These variations are attributed to input and removal processes coupled with large sulphur isotope selectivity during bacterial SO_4^{2-} reduction. Other marine sulphate minerals are also enriched in ^{34}S . In the case of barites, some massive occurrences may resemble isotopically contemporaneous seawater sulphate, whereas barite nodules may have $\delta^{34}S$ values exceeding +80 as the consequence of sulphate reduction on a very localized scale (Sakai 1971; Cecile et al. 1983).

2.4 SULPHUR ISOTOPE COMPOSITION OF FOSSIL FUELS

It is expected that fossil fuels should have nearly the same S isotope composition as the plants and animals from which they were derived, with possible loss of the lighter isotopes during maturation. It turns out, however, that the S content of fossil fuels may be considerably higher than that of the source living matter. This enrichment cannot be explained by loss of organic matter during decay and burial. Hence, in addition to SO_4^{2-} assimilation which produces vital S amino acids, sulphide from dissimilatory bacterial sulphate reduction must be incorporated into the decaying organic matter.

Low S-containing coals (<1% S) tend to have $\delta^{34}\text{S}$ values between 0 and +10, consistent with relatively fresh, water environments for the original living matter. Higher S-containing coals may reflect a greater marine influence. Whereas assimilated S in the original plants would be more enriched in ^{34}S , bacteriogenic sulphide would also influence the system. Hence, high S-containing coals tend to vary widely in their sulphur isotope composition in response to within-seam variations in the distribution and isotope composition of organic S and finely disseminated and massive pyrite (Smith and Batts 1974; Price and Shieh 1979).

Most oils form in a marine environment and so seawater SO_4^{2-} is the main source of S in petroleum. Since petroleum tends to be depleted in ^{34}S with respect to its marine SO_4^{2-} source, the bacterial reduction mechanism appears to dominate. Otherwise, the S forms in petroleum should have nearly the same isotopic composition as marine SO_4^{2-} , because fractionation during assimilation by plants and animals is small.

The hydrogen sulphide that co-exists with oils often has the same sulphur isotope composition as the oils (Thode et al. 1958). However, deep sour gas occurrences where H_2S may constitute greater than 90% of the total gas, tend to have $\delta^{34}\text{S}$ values close to those of anhydrites in their carbonate reservoirs (Orr 1974; Krouse 1977a). This is believed to reflect thermochemical reduction of SO_4^{2-} with negligible sulphur isotope selectivity. Sour gas processing is a major industry in the Province of Alberta, Canada. Emissions of sulphur oxides enriched in ^{34}S (+15 to +30‰) arise from the use of the Claus reaction to produce elemental sulphur. This coupled with estimated pre-industrial environmental receptor $\delta^{34}\text{S}$ values ranging from 0 down to -30‰ has provided effective environmental sulphur isotope tracer experiments on a large scale. This "isotopic leverage" is the "heart" of this current review. It is also interesting that some soils in Australia are becoming enriched in ^{34}S because of applications of fertilizers derived from the Alberta sour gas industry (J.R. Freney, private communication 1984).

3. OXYGEN ISOTOPE ABUNDANCES IN SULPHATES IN RELATION TO THE SULPHUR CYCLE

3.1 INTRODUCTION

Oxygen isotope ratio measurements are uniquely applicable to the study of mechanisms of formation of natural or man-made sulphates in the environment because the $^{18}\text{O}/^{16}\text{O}$ ratios of sulphates that are formed from given reactants (sulphur oxides, water, and oxidants) can differ, depending upon the mechanisms by which they are formed. Some of the more prominent mechanisms of formation of SO_4^{2-} from SO_2 are aqueous-phase O_2 oxidation, aqueous-phase peroxide oxidation, and high-temperature oxidation to SO_3 (in combustion sources), followed by hydration to H_2SO_4 . Microorganisms such as *Thiobacillus* are able to oxidize sulphide and S^0 to SO_4^{2-} . Once formed, sulphates are extremely stable with respect to oxygen isotopic exchange with water, with which they may be subsequently associated.

The use of oxygen isotopes for determining sources of sulphate relies on the following assumptions: (1) the rate of isotopic exchange between dissolved sulphate and water is very slow; (2) the rate of isotopic exchange between SO_2 and associated water in either the vapour or liquid phase is rapid; (3) SO_3 formed by high-temperature oxidation of SO_2 hydrates rapidly to form H_2SO_4 ; and (4) the differences in oxygen isotopic compositions of environmental water and oxidants are usually large. With reference to point (4), the $\delta^{18}\text{O}$ values* of atmospheric O_2 , seawater, and atmospheric vapour are +23, 0, and -30 to -60‰, respectively (Horibe et al. 1973).

3.2 OXYGEN ISOTOPE EXCHANGE BETWEEN SULPHUR OXIDES AND H_2O

3.2.1 $\text{SO}_4^{2-} - \text{H}_2\text{O}$

Measurements of isotope exchange factors between water and dissolved sulphate, as functions of temperature and pH, indicate that under typical ambient conditions, the rate of isotope exchange is extremely slow (Lloyd 1967; Kusakabe and Robinson 1977; and Chiba and Sakai 1985). For example, it is evident from kinetic data presented by Lloyd (1967) that even in highly acidic rain of pH~4, the half-time of oxygen atom exchange between sulphate and water is of the order of 1000 years. Therefore, once sulphate is formed, its $\delta^{18}\text{O}$ value is preserved. Further, the $\delta^{18}\text{O}$ of the sulphate is not appreciably affected by the heat treatments in acidified solutions that are necessary in analytical procedures for the precipitation of BaSO_4 (Holt et al. 1978).

Despite the above statements, equilibrium exchange between SO_4^{2-} and H_2O is considered by some authors to have occurred in some geothermal areas. On this assumption, temperatures were derived from the isotopic compositions in springs at Wairakei, New Zealand (~270°C; McKenzie and Truesdell 1977) and for wetstream wells at Larderello, Italy (~240°C; Cortecchi 1973). Because of their unusually rapid ascent to the surface,

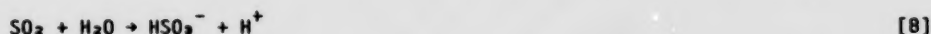
$$\delta^{18}\text{O} = \left\{ \frac{[^{18}\text{O}/^{16}\text{O}]_X}{[^{18}\text{O}/^{16}\text{O}]_{\text{SMOW}}} - 1 \right\} \times 10^3$$

SMOW: Standard Mean Ocean Water

some Yellowstone thermal waters indicate a sulphate-water oxygen isotope temperature of about 360°C without having reequilibrated during ascent.

3.2.2 $\text{SO}_2 - \text{H}_2\text{O}$

When SO_2 dissolves in water, it rapidly hydrolyzes according to the chemical reaction,



(Eigen et al. 1961; Beilke and Gravenhorst 1978). Isotopic equilibration is very fast, so that, in the atmosphere or hydrosphere, the HSO_3^- isotopically equilibrates with liquid water. Since the H_2O is in excess, upon oxidation the original $\delta^{18}\text{O}$ of the SO_2 is not reflected in the $\delta^{18}\text{O}$ of the sulphate product (Holt et al. 1981). Rather, the $\delta^{18}\text{O}$ of three of the oxygens in the sulphate product should be strongly controlled by the $\delta^{18}\text{O}$ of the H_2O because of reaction [8].

In SO_4^{2-} preparations by Fe^{3+} -catalyzed aqueous air oxidation with water in large excess, Holt et al. (1981) observed that the $\delta^{18}\text{O}$ of the SO_4^{2-} varied with the $\delta^{18}\text{O}$ of the water according to regression curves of the general form,

$$\delta^{18}\text{O}_{\text{SO}_4^{2-}} = \sim \frac{3}{4} \delta^{18}\text{O}_{\text{H}_2\text{O}} + C_1 \quad [9]$$

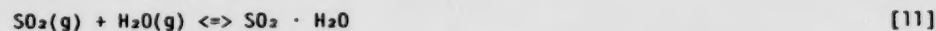
The slope of $\sim 3/4$ suggests that indeed three of the four oxygens in the sulphate are isotopically controlled by the water. In other experiments in which the $\delta^{18}\text{O}$ of the water was held constant, the $\delta^{18}\text{O}$ of the sulphate remained constant even though the $\delta^{18}\text{O}$ of the SO_2 was varied. This confirmed that the isotopic composition of the SO_2 was erased by hydrolysis in excess water before oxidation to SO_4^{2-} .

Rapid isotopic equilibration between H_2O and dissolved SO_2 was further demonstrated when SO_2 was oxidized by H_2O_2 in aqueous solution. The $\delta^{18}\text{O}$ of the SO_4^{2-} varied with that of the water according to the relation,

$$\delta^{18}\text{O}_{\text{SO}_4^{2-}} = \sim \frac{3}{5} \delta^{18}\text{O}_{\text{H}_2\text{O}} + C_2 \quad [10]$$

The $3/5$ slope suggests that three of the five oxygens in the intermediate adduct $\text{HSO}_3^- \cdot \text{H}_2\text{O}_2$ were isotopically controlled by the solvent water, two by the oxidant, and essentially none by the SO_2 (Holt et al. 1981b).

Rapid isotopic equilibration between SO_2 and water vapour was also demonstrated in a series of experiments (Holt et al. 1983). The isotopic equilibration apparently occurs in the reaction



Rapid isotopic equilibration between SO_2 and water vapour means that in SO_2 - O_2 - H_2O vapour mixtures, in which water vapour is in excess (as in the atmosphere), the $\delta^{18}\text{O}$ of the SO_2 is changed from that at its point of origin; it is dynamically controlled by the $\delta^{18}\text{O}$ of the associated water vapour.

3.2.3 Hydration of SO_2

Sulphur trioxide is formed at high temperatures in exhaust gases from smelters, power plants, combustion engines, etc. As the exhausted gases cool, the SO_3 rapidly reacts with combustion-produced water vapour. Since the combustion-produced water vapour is relatively high in $\delta^{18}\text{O}$ because of isotopic equilibration with air O_2 , the hydrated sulphuric acid that is formed has a relatively high $\delta^{18}\text{O}$.

3.3 KINETIC ISOTOPE EFFECTS

3.3.1 SO_4^{2-} Reduction

Bacteria preferentially metabolize ^{16}O in the reduction of SO_4^{2-} to H_2S . This leaves the remaining SO_4^{2-} heavier in $\delta^{18}\text{O}$ according to the relationship,

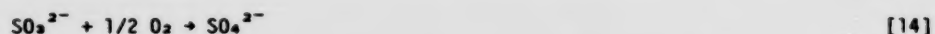
$$\delta - \delta_0 = 1000 (1 - \alpha) \ln F \quad [12]$$

where F is the fraction reacted; δ and δ_0 are the $\delta^{18}\text{O}$ values for unreduced and initial sulphate, respectively. Lloyd (1967) found that $1000(1 - \alpha) = 4.6\text{‰}$. Mizutani and Rafter (1969a) reported that the ratio of $\delta^{18}\text{O}$ to $\delta^{34}\text{S}$ for the remaining SO_4^{2-} was approximately 1:4. This observation is interesting because of the 1 sulphur atom to 4 oxygen atoms in the SO_4^{2-} structure. However, the same authors (1973) found departures from this ratio when waters of different $\delta^{18}\text{O}$ values were used for the medium. The $\delta^{18}\text{O}$ of the remaining sulphate was a function of the $\delta^{18}\text{O}$ of the water, whereas the $\delta^{34}\text{S}$ was independent of this. The rate of exchange between SO_4^{2-} and H_2O is extremely slow under the conditions of their experiments. Therefore, it was concluded that the isotopic composition of SO_4^{2-} was altered by back reaction of intermediates which had exchanged oxygen isotopes with H_2O .

The $\delta^{34}\text{S}:\delta^{18}\text{O}$ ratio of 4:1 has been found in laboratory experiments (Hunt 1974) and natural settings (Rafter and Mizutani 1967). However, ratios of closer to unity were found in stratified lakes in the Canadian Arctic (Jeffries et al. 1985).

3.3.2 Sulphide Oxidation

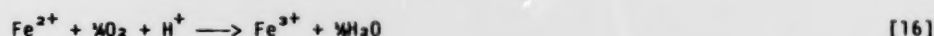
Lloyd (1967), using Na_2S solution through which oxygen was bubbled, suggested that the inorganic oxidation of sulphide to sulphate takes place according to the following reactions:



* Note that this equation was not balanced with respect to hydrogen in the reference.

He found that the incorporation of the O_2 followed the relation $\delta - \delta_0 = 1000(1 - \alpha) \ln F$, where $1000(1 - \alpha) = 8.7^\circ/\text{‰}$, so that lighter oxygen was preferentially consumed. He also found that there was no oxygen isotope selectivity during the incorporation of water oxygen. Lloyd asserts that two-thirds of the oxygen comes from water and one-third from molecular oxygen. However, the stoichiometry of the above mentioned equations seemingly belie this assertion. It appears that the intermediate SO_4^{2-} exchanges oxygen with water and in the final product there are effectively two parts of water oxygen and only one part of air oxygen.

Taylor et al. (1984) cited three reactions identified with the oxidation of FeS_2 :



In reaction [15], all sulphate oxygen is derived from water molecules, whereas in reaction [17], 87.5% of the sulphate oxygen is derived from molecular oxygen and 12.5% from water molecules. Sulphates produced by the two reactions have different $\delta^{18}O$ values because of the generally large difference between the $\delta^{18}O$ values of O_2 and H_2O . Taylor et al. (1984) plotted $\delta^{18}O$ values for SO_4^{2-} in acid mine waters against those of associated H_2O and on the basis of theoretical lines, estimated the relative contributions of the above reactions. Van Everdingen and Krouse (1985) examined their plots and found them to be in error. The corrected plot is shown in Figure 4.

3.4 OXYGEN ISOTOPE COMPOSITION OF TERRESTRIAL SULPHATES

3.4.1 Marine Sulphate

A number of measurements have shown that the ^{18}O content of sulphate throughout the modern ocean is constant, with a $\delta^{18}O$ of $+9.6^\circ/\text{‰}$. This means that oceanic SO_4^{2-} and ocean H_2O are not in oxygen isotope equilibrium. Lloyd (1968) proposed a steady state model based on his measurements of kinetic isotope effects. He assumed that oxygen incorporated in sulphate during sulphide oxidation was one-third derived from atmospheric O_2 ($+23^\circ/\text{‰}$) and two-thirds from the ocean H_2O ($0^\circ/\text{‰}$). A kinetic isotope effect of $-8.7^\circ/\text{‰}$ was associated with the uptake of atmospheric O_2 . In combination with an ^{18}O enrichment in residual SO_4^{2-} of $4.5^\circ/\text{‰}$ during bacterial SO_4^{2-} reduction, Lloyd's steady state model predicted the $\delta^{18}O$ value of oceanic SO_4^{2-} to be $+9.1^\circ/\text{‰}$, not far from the observed $+9.6^\circ/\text{‰}$.

Cortecci and Longinelli (1971, 1973) found the ^{18}O content of sulphate in the shells of living marine organisms to be close to that of the SO_4^{2-} in the water in which they grow. They also found, however, that fossil shells exhibit a wide range of sulphate oxygen isotopic compositions which they attributed to postdepositional changes. Thus, they concluded that the ^{18}O content of sulphate from shells gives no information on past ocean sulphate $\delta^{18}O$ values.

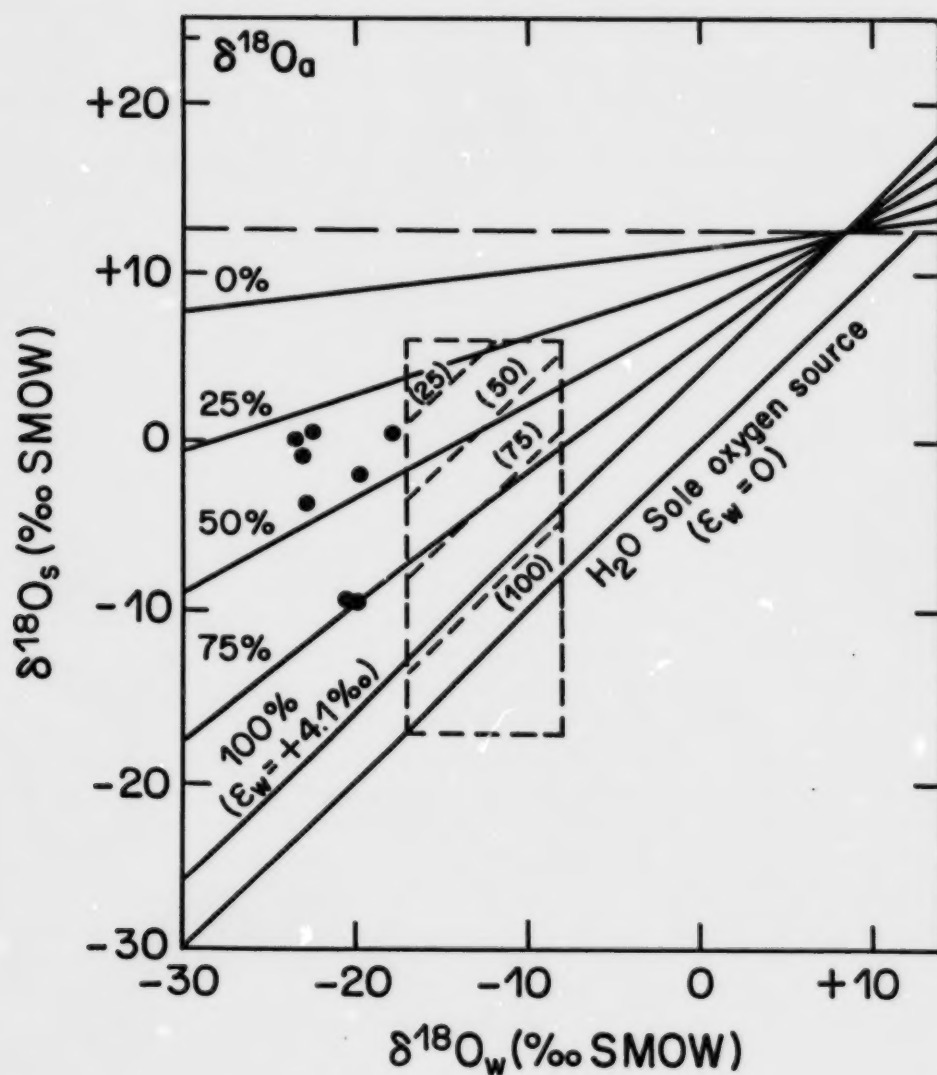


Figure 4. Predicted relationships between $\delta^{18}\text{O}$ values for secondary sulphates produced by oxidation of pyrite and those of associated water (taken from van Everdingen and Krouse 1985). The percent contributions of equation [8] are shown on the lines. The broken lines are those of Taylor et al. (1984).

As with sulphur isotopes (Section 2.1), the oxygen isotope composition of the oceans has fluctuated over geological time (Figure 5). The bulk of the data has been derived from evaporite studies (Holser et al. 1979; Shakur 1982). Massive barites and some bedded barites without significant organic matter have $\delta^{18}\text{O}$ values close to the oceanic curve (Cecile et al. 1983). Barite nodules, however, may be unusually enriched in ^{18}O as the result of sulphate reduction on a localized scale.

3.4.2 Surface Waters

The $\delta^{18}\text{O}$ values of sulphates in streams and lakes vary depending on natural and anthropogenic inputs and on bacterial activity. For example, Longinelli and Cortecci (1970) found that the $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, and concentration of the sulphates generally increased downstream along the course of the Serchio River in Italy.

Isotopically, the sources of sulphates in surface waters comprise two main groups: SO_4^{2-} enriched in ^{18}O (and ^{34}S) derived from evaporite minerals and SO_4^{2-} depleted in ^{18}O (and ^{34}S) derived from reduced sulphur sources such as sulphide and organic sulphur. An additional source enriched in ^{18}O , but varying in ^{34}S , is atmospheric sulphate generated in high temperature combustion (Section 3.2.3).

3.4.3 SO_4^{2-} in Precipitation

Isotopic analyses of SO_4^{2-} in precipitation have led to at least two significant observations. First, the $\delta^{18}\text{O}$ of SO_4^{2-} varies seasonally and in phase with corresponding isotopic variations of the precipitation water (Cortecci and Longinelli 1970; Longinelli and Bartelloni 1978; and Holt et al. 1981a). Holt et al. (1979a) noted that in samples collected at Argonne, Illinois, the amplitude of the seasonal variation of $\delta^{18}\text{O}$ in precipitation sulphate was $\sim 3/4$ of that of the precipitation water. This suggests that three of the four oxygens in precipitation sulphate are controlled by the precipitation water and, therefore, essentially complete isotopic equilibration occurs between the precipitation water and dissolved HSO_4^- prior to significant oxidation to SO_4^{2-} .

The second observation is that at receptor sites near sea coasts, the $\delta^{18}\text{O}$ may be significantly affected by sea spray (Mizutani and Rafter 1969b; Cortecci and Longinelli 1970). Other sources of excess sulphate in rainfall, particularly in arid regions, may be the dispersion of mineral sulphates by wind from evaporite deposits at the surface or from sulphate minerals which have precipitated from terrestrial surface water in playas or saline environments, or in soils.

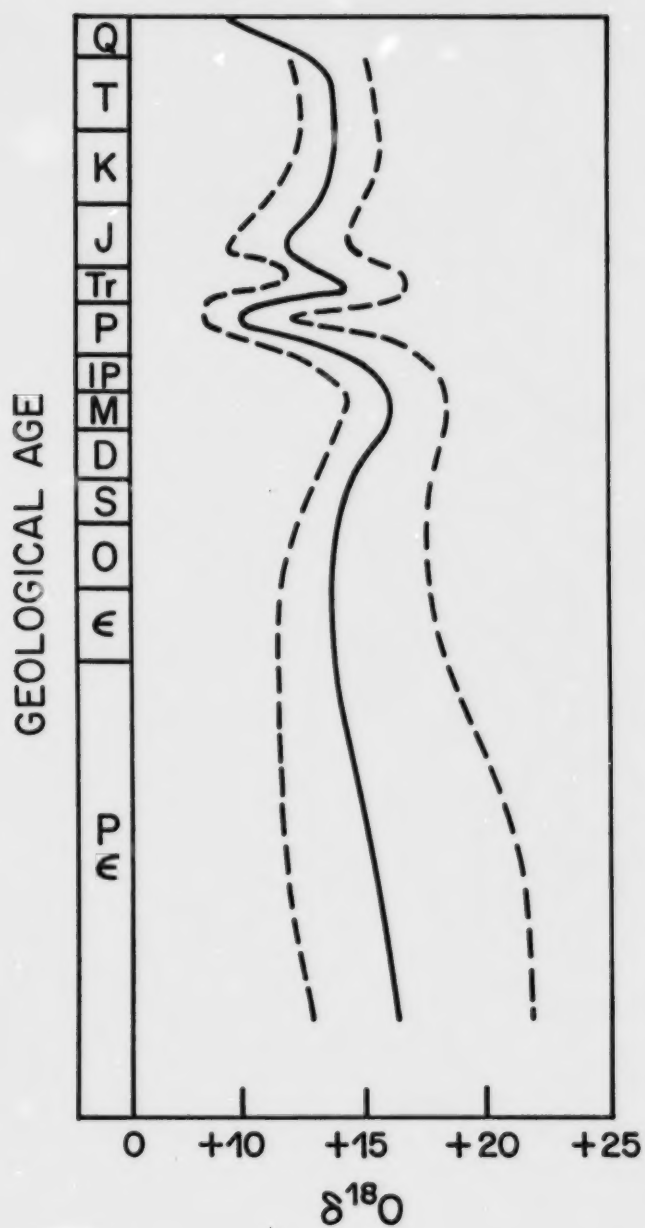


Figure 5. $\delta^{18}\text{O}$ in oceanic sulphate over geological time. Solid line indicates mean; dashed lines indicate range.

4. SULPHUR ISOTOPE COMPOSITION OF ENVIRONMENTAL RECEPTORS

4.1 ATMOSPHERE

4.1.1 Introduction

Sulphur inputs, transformations, and removal from the atmosphere can potentially be assessed by the measurement of the isotopic abundances of sulphur (and oxygen; Section 3.4.3) associated with its compounds. The major inputs comprise anthropogenic and biogenic activities and sea spray. Transformations arise from oxidation, neutralization, and other chemical reactions. Advection causes dilution and the main removal processes are dry deposition (controlled by gravitation and diffusion) and rain. The admixture of sources can be discerned from their isotopic signatures, whereas transformations and removal can be followed from the isotopic fractionation that might occur thereafter.

In this section, the atmospheric sulphur cycle and the chemistry pertaining to it are summarized. Also presented is information on natural isotopic variations and fundamental concepts relating to the use of isotopic data to delineate anthropogenic S in the atmosphere.

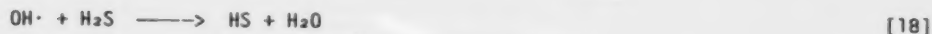
4.1.2 Sulphur Species in the Atmosphere and Related Chemistry

Sulphur in the atmosphere occurs in the gaseous (H_2S , DMS, DMDS, COS, CS_2 , SO_2), liquid (H_2SO_3 , SO_4^{2-} , SO_3^{2-}), and solid (sulphates, S^0) phases.

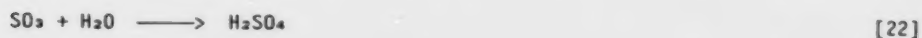
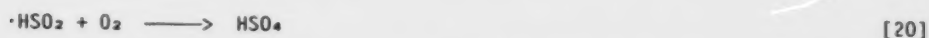
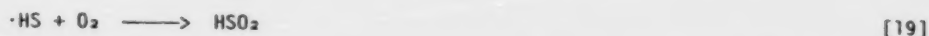
The chemistry of sulphur in the atmosphere is complex. The reduced S-compounds are subject to direct photochemical oxidation and all are to some degree subject to attack by other photochemically produced species including ozone and the OH radical. Cox and Sheppard (1980) have summarized reaction rates of SO_2 , H_2S , and organic sulphides with OH radicals in the troposphere. A simplified summary of oxidative reactions follows. Much of this material has been abstracted from a review by Newman (1984).

4.1.2.1 H_2S Oxidation. There are a variety of possible reactions for the destruction of atmospheric H_2S . Sprung (1974) gave rates for a variety of homogeneous gas phase reactions. Hydroxyl radical is the most important destroyer of H_2S , followed at a rate three orders of magnitude lower by ozone.

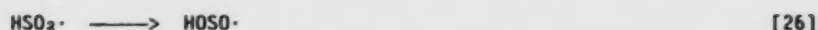
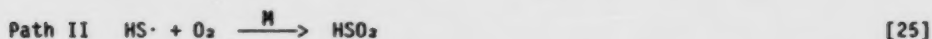
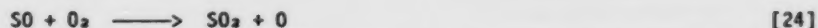
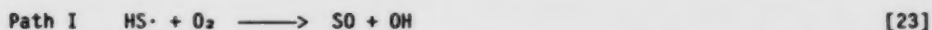
The reaction of H_2S with OH radical leads to the formation of HS radical and water.



The HS radical may react with O_2 to form SO_2 , or may proceed directly to sulphuric acid (Thiemens 1977).



Thiemens and Schwartz (1978) have shown that the HS radical goes quantitatively to SO₂ by one of two paths:



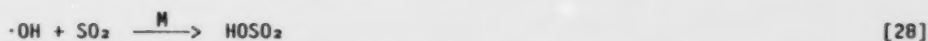
For either path, all of the oxygen in the resultant SO₂ comes from atmospheric O₂.

Hales et al. (1974) examined the heterogeneous oxidation of H₂S by ozone and concluded that heterogeneous processes on the surface of their reactors were unimportant and that, similarly, heterogeneous oxidation is probably unimportant in the atmosphere. Chen and Morris (1972) measured the rates of H₂S oxidation of O₂ in solution and found that at pH values below 6, the oxidation rate is negligible. It appears that heterogeneous oxidation of the H₂S is unimportant compared to the homogeneous, OH radical reaction.

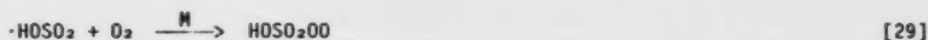
4.1.2.2. SO₂ Oxidation. Since most of the anthropogenic emissions are in the form of SO₂ and since biogenic sulphides are oxidized to SO₂, the chemistry of SO₂ in the atmosphere is of major importance. Garland (1978) estimated that about half of the SO₂ emitted to the atmosphere is removed by dry deposition; the remaining half is removed by wet deposition. The conversion of SO₂ to sulphate comprises oxidation, hydration, and condensation. These processes may occur in a variety of sequences.

Newman (1981) reviewed the literature on the atmospheric oxidation of sulphur dioxide in relation to power plant and smelter plume studies. The average rate of oxidation is generally less than 1% per hour in clean air, but in polluted air the rate can easily double. A diurnal variation in the rate of oxidation is observed that is near zero at night and approximately 3% per hour during midday. There is no basis for a choice between the homogeneous or the heterogeneous pathway as the dominant oxidation mechanism.

Eggleton and Cox (1978) have reviewed the homogeneous oxidation of SO₂ in the atmosphere. The most important reaction in both polluted and unpolluted air is reaction with free radicals, especially OH radical.

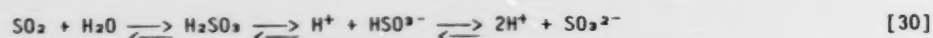


Calvert et al. (1978) concluded that the most likely reaction of the HOSO₂ radical will be with O₂:



They also noted that the disproportionation reaction forming HO_2 and SO_3 is endothermic and, therefore, non-competitive with the preceding reaction. The resulting HOSO_2OO radical is an extremely reactive species which should eventually gain a hydrogen atom and lose an oxygen atom to become H_2SO_4 , or lose both an oxygen and a hydrogen atom to become SO_3 which would then hydrate to H_2SO_4 . The H_2SO_4 can then be neutralized by ambient ammonia, ultimately to form $(\text{NH}_4)_2\text{SO}_4$. Davis et al. (1978) have estimated the rates of a variety of reactions involving HSO_3 and HSO_3 radicals. They believe that the dominant processes are the oxidation of HSO_3 radical to HSO_3 radical by atmospheric O_2 with a slightly slower rate for the hydration of HSO_3 radical. The resulting HSO_3 radical is hydrated (probably with several water molecules) at a rate several orders of magnitude greater than any competing reaction. It is not clear at what point the reactions can be considered to change from homogeneous gas phase reactions to heterogeneous solution reactions.

The heterogeneous oxidation of SO_2 in solution has been reviewed by Beilke and Gravenhorst (1978) and by Hegg and Hobbs (1978). The primary step in these reactions is the solution of SO_2 in water and its equilibration in the sulphurous acid system to form bisulphite and sulphite.



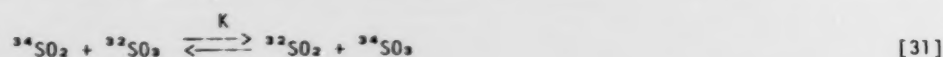
The dissociation reactions are very fast (order of 10^8 s^{-1}). In solution, SO_3^{2-} ion is present in negligible amounts at pH values less than 6 and the system in rain and cloud droplets is dominated by the bisulphite ion.

The oxidation of S from the +4 to the +6 valence state in droplets may proceed by three major mechanisms: oxidation by O_2 without metal catalysts; oxidation by O_2 in the presence of transition metal catalysts; and oxidation by strong oxidants, particularly ozone or hydrogen peroxide. Beilke and Gravenhorst (1978) concluded that at the pH values expected in droplets, the uncatalyzed reaction with O_2 is unimportant. The catalyzed reaction may be important where the transition metal component in the solution is extremely high, but oxidation by ozone and hydrogen peroxide is probably the dominant mechanism. Hegg and Hobbs (1978) suggested that some mixed salt catalysts (equimolar Mn^{2+} and Fe^{3+}) may cause oxidation of SO_2 in urban atmospheres. Newman (1979) has suggested that oxidation within cloud droplets is an important means through which air obtains its sulphate and acidity, and evidence has been gathered to substantiate this hypothesis (Daum et al. 1983).

4.1.3 Sulphur Isotope Fractionation During Atmospheric Reactions of S-Compounds

In order to use sulphur isotopes as a tracer of sulphurous emissions in the atmosphere, a requirement is that the isotopic selectivity during chemical conversions be minimal. Therefore, possible exchange reactions and kinetic isotope effects should be examined.

Once into the atmosphere, exchange between gaseous species should be minimal because of the dilution. Within the industrial source this may not be true. For example, the temperature dependence of the equilibrium constant for the exchange reaction,



has been used to try to locate the site of SO_2 formation in a combustion process (Newman et al. 1973).

Sulphur isotope fractionation during oxidation of H_2S and SO_2 appears to be minimal as found for sampling near biogenic H_2S emitters (e.g., Krouse and van Everdingen 1984) and power plant plumes (Newman et al. 1975). In the case of the latter, there tended to be a small decrease in $\delta^{34}\text{S}$ in SO_2 with distance downwind of the power plant stack. Newman et al. (1975) interpreted these data in terms of a pseudo-second-order mechanism which depended upon SO_2 and particulate concentrations. In such studies, it is difficult to determine the extent of reaction, the main problem being that, with distance from the stack, contributions of S-compounds arise from other sources. One approach is the injection into the stack of a conservative tracer such as SF_6 (Newman et al. 1975) or gold dust (Rowe 1976).

A small decrease in $\delta^{34}\text{S}$ in SO_2 with distance downwind of a sour gas processing plant has also been noted (Figure 6).

4.1.4 Sampling of Atmospheric S-Compounds

The first requisite for sampling sulphur compounds from the atmosphere for isotopic measurements is the preservation of their isotopic ratio. Concentrations in the atmosphere can be quite low (parts per billion or less) and the sampling has to be appropriate to obtain enough material in a time period commensurate with the temporal resolution dictated by the experiment. At least one milligram of material is required to perform a precise isotopic ratio measurement on the mass spectrometer. Further, it is generally desirable to sample and measure the isotopic ratio for each of the sulphur substances present in the atmosphere. A further requisite is to prevent transformation of one sulphur compound into another, e.g., preventing the conversion of SO_2 to sulphate when measuring the isotopic ratio of the sulphate particles in the atmosphere.

Huygen (1963) successfully collected SO_2 by forcing air through cellulose filters impregnated with potassium hydroxide plus glycerol or triethanolamine. This procedure was further developed by Forrest and Newman (1973), who collected ambient samples with a filter pack arrangement consisting of a quartz prefilter to trap aerosol sulphate followed by the hydroxide impregnated filter paper to absorb SO_2 . Thus, they were able to achieve air flow rates of $2 \text{ m}^3 \text{ min}^{-1}$ with 8×10 inch (20.3×25.4 cm) filters in high-volume samplers.

Sulphur isotope analyses can also be carried out on lead peroxide-treated paper placed on the inner surface of an open cylinder which is exposed vertically to the atmosphere typically for one month periods. Krouse (unpublished data, 1976) found isotope data from these cylinders to be comparable to those obtained using the filter pack of Forrest and Newman (1973).

Particulates may also be collected according to aerodynamic size using stacked metal plates with either staggered holes or slots (slotted cascade impactor). Commercial units have typically five aerodynamic size classes: >7 , 3.3 to 7.0, 2.0 to 3.3, 1.1 to 2.0, and $1.0 \times 10^{-6} \text{ m}$. These are considered to correspond to particles found on the human skin surface and in the trachea and primary bronchi, secondary bronchi, terminal bronchi, and alveoli, respectively. It is expected that the smaller sized particles can potentially come from a greater distance.

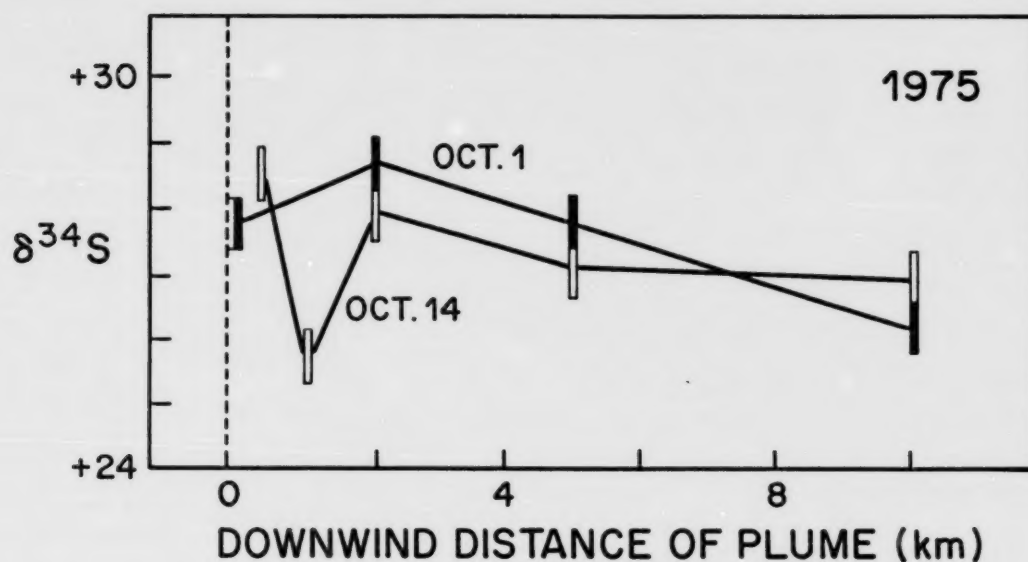


Figure 6. $\delta^{34}\text{S}$ values versus downwind distance of SO_2 in a sour gas processing plant plume at Crossfield, Alberta, 1975. High volume sampling of the plume was carried out with a helicopter. Vertical bars represent estimated measurement errors.

Concentrations of atmospheric S-compounds and their isotopic composition at an observation point are dependent upon wind direction. Consequently, if samples can be characterized according to wind direction, more information might be obtained on sources and mixing phenomena. Data can be depicted on a polar diagram with $\delta^{34}\text{S}$ values or concentrations and wind direction plotted as the radial and angular co-ordinates, respectively (Figure 7). It must be emphasized that the data for Figure 7 were collected using one sampler with concurrent meteorological data and interpretations were made after the fact. This procedure is inefficient because the wind direction might change many times during the acquisition of a sample. In other words, the construction of Figure 7 was possible because the particular major synoptic event was not subject to large, short-term fluctuations. Consequently, an array of high-volume samplers, each of which responds to a preselected wind direction, was conceived.

An array with four high-volume samplers was tested in 1976 on the same scaffold in the Whitecourt area (Krouse et al. 1984). The array was programmed by a simple electrical contact system within the head of the wind vane, and some difficulties were experienced at low wind velocities because of internal friction. Nevertheless, the observations were similar to those recorded the previous year during a major synoptic event.

The four-unit sampler array was also used for ground level sampling in the Teepee Creek area of Alberta (Krouse and Case 1981). Although there was a minor source of industrial emissions in the area, it was found that the highest SO_2 concentrations were not downwind of the plant. Further, a SO_2 flux appeared to move through the study area.

A mobile nine-unit, high-volume sampler array was then built and tested. Eight samplers were individually triggered according to preselected wind sectors, whereas the ninth was directionally independent and operated at wind speeds below a pre-set cutoff. An elapsed time counter on each sampler recorded its accumulated time of operation. Since airflow through each sampler was calibrated and controlled, the amount of air which had passed through the sample could be determined and used in concentration calculations. Filters would not be removed from a sampler which had operated for an insufficient time.

A criticism of the mobile array is that winds aloft are seldom in the same direction as those at ground level. Therefore, to avoid false source identification, the elevational dependence of the wind behaviour must be known. The argument can be reversed by noting that the isotope determinations per se help to differentiate sources and reduce interpretation errors. It would also seem that concentration and isotope measurements of atmospheric-S at "nose level" are justified from the viewpoint of human health.

4.1.5 Further Characterization of Particulates

The size of particulates relates to their source, accretion, and transport in the atmosphere. Particles combining lowest density and lowest size arriving at an observation point can potentially come from further distances. Therefore, if different $\delta^{34}\text{S}$ values are found for different size fractions, it would seem that different sources are involved. Aerodynamic sizing with a 5 stage slotted cascade impactor was incorporated in the mobile array described above (Krouse and Case 1984). Some of the data

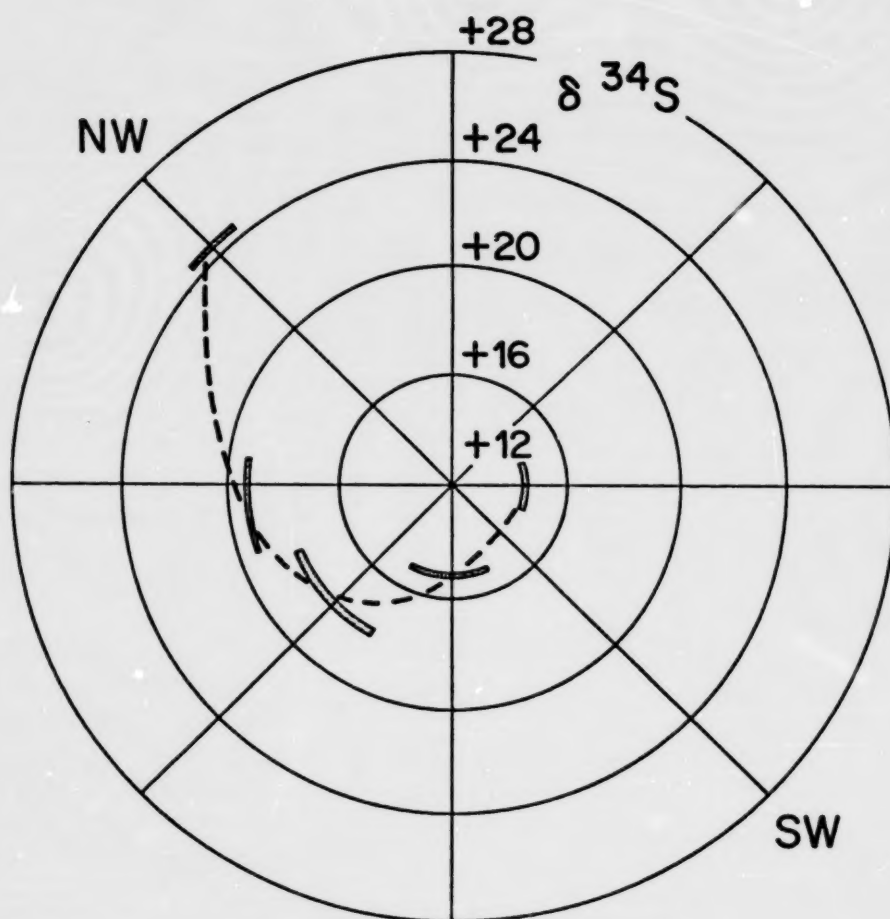


Figure 7. Polar diagram depicting the dependence of $\delta^{34}\text{S}$ of SO_2 on wind direction, West Whitecourt Case Study, 1975. A sour gas processing plant is northwest of the sampling location (taken from Krouse et al. 1984).

obtained with this unit are presented in Table 1. It is seen that the smallest particles are significantly depleted in ^{34}S in comparison to those $> 1\mu$, indicating that they are not related to the nearby industrial emitter.

If more parameters are examined for particulates, more unknowns in terms of sources can be identified. Visual examination is obviously desirable. The diverse nature of particulates which may include dust particles as well as biological materials such as pollen grains and broken plant debris, can be seen in scanning electron microscope (SEM) photographs (Krouse et al. 1984). Variations in $\delta^{34}\text{S}$ values of total particulate with sampling height can be explained by differing mixtures of abiological and biological matter (Krouse et al. 1984).

4.1.6 Elucidation of Sources, Mixing, and Dispersion Using Isotope and Concentration Data

Plots of $\delta^{34}\text{S}$ values versus various functions of concentration can prove effective for identifying sources and monitoring the fate of atmospheric sulphur pollutants (Section 1.3). A number of hypothetical source combinations were examined by Krouse (1980). The conceptual and mathematical analyses assumed complete mixing without any isotope fractionation. In principle, the conclusions are valid for gases, ions, and fine particulates in fluids.

In the atmosphere, a frequently encountered situation is a source "A" which is relatively constant in its emission rate and $\delta^{34}\text{S}$ value for a few hours or days, but upon which is superimposed a source "B". The latter might be varying in emission rate at a different fixed $\delta^{34}\text{S}$ value. The former might be the "background" and the latter an industrial stack. The lowest concentration corresponds to contributions from source "A" only. With increasing concentration, the contribution from "B" increases so that the $\delta^{34}\text{S}$ value approaches that of "B" at very high concentrations. It was shown in this case that a plot of $\delta^{34}\text{S}$ versus the reciprocal of concentration is linear, the y-intercept corresponding to the $\delta^{34}\text{S}$ value of the variable emitter "B" (Section 1.3). This model applies over short periods of time because, generally, the background conditions do not remain constant due to factors such as changing wind direction and fluctuations in biological emissions. Such a plot was generated for emissions from the Crossfield sour gas plant during a shutdown-startup event (Krouse 1980, Figure 8).

If the area surrounding a dominant industrial emitter is examined randomly on many occasions, the data tend to fit a pattern such as that shown in Figure 9.

The spread in $\delta^{34}\text{S}$ values at low concentrations reflects many minor sources at different locations. These sources are not evident at higher concentrations which are dominated by the industrial source. A given point on the graph is primarily a function of wind direction which determines the relative contributions from the various sources. In turn, biological activity may impose a seasonal dependence upon some sources.

4.1.7. Sulphur Isotope Abundance Variations in Atmospheric S-Compounds

The S-compounds in the atmosphere can originate naturally (volcanic, sea spray, aeolian weathering, biogenic) or anthropogenically (combustion and refining of fossil fuels, gypsum processing, ore smelting). This section summarizes sulphur isotope data pertaining to the various origins of atmospheric S-compounds.

Table 1. $\delta^{34}\text{S}$ values for SO_2 and six aerodynamic class sizes of airborne particulate matter near Crossfield, Alberta, March to April 1983 (Krouse and Case 1984).

Aerodynamic Size (μ)	Sampler			
	1	2	3	4
7.0	+18.8	+14.0	+16.6	+19.4
3.3 to 7.0	+13.2	+12.0	+ 6.5	+17.1
2.0 to 3.3	+15.3	+13.6	+14.5	+16.0
1.1 to 2.0	+13.1	+ 9.5	+15.5	+15.6
1.0	+12.3	+13.5	+18.9	+16.6
<1	- 2.0	- 3.4	+ 3.5	+ 6.1
SO_2	+23.4	+22.4	+15.2	+16.3

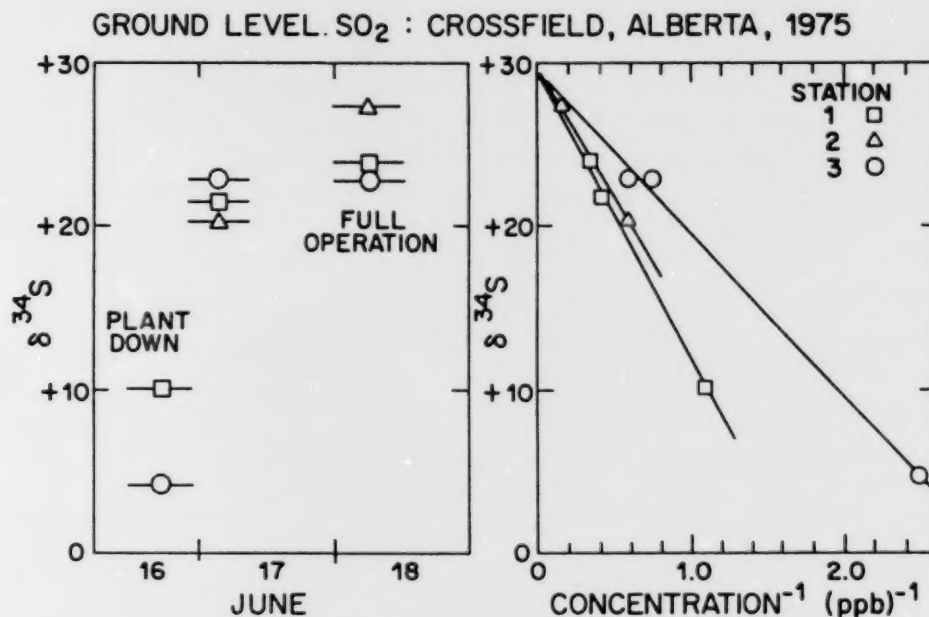


Figure 8. Isotopic monitoring of a sour gas plant start-up with ground level, high-volume sampling of atmospheric SO_2 , Crossfield, Alberta, 1975 (taken from Krouse 1980). As the operation commenced, the $\delta^{34}\text{S}$ value and the concentration of SO_2 in the air increased. Horizontal lines correspond to duration of sampling. Plotting $\delta^{34}\text{S}$ versus $\text{concentration}^{-1}$ gives linear trends which extrapolate to a $\delta^{34}\text{S}$ value near +29‰ on the y-axis. This extrapolated value was identical with the $\delta^{34}\text{S}$ value of the plume obtained using high-volume sampling from a helicopter. Three linear plots arise because the contributions of SO_2 from other sources differed at the three stations denoted by different symbols.

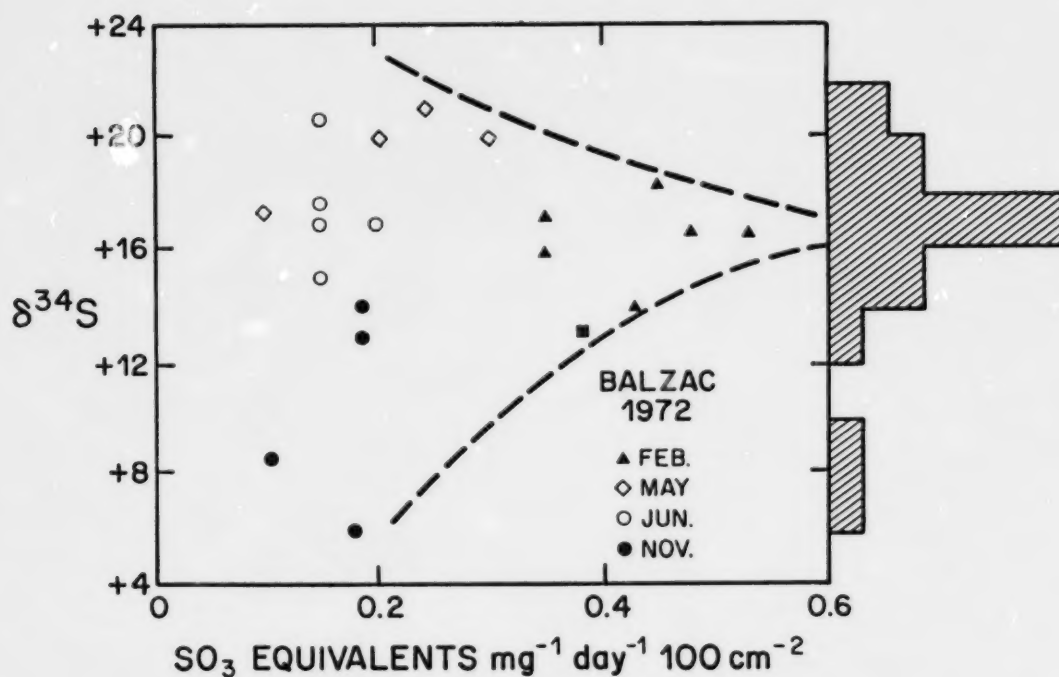


Figure 9. $\delta^{34}\text{S}$ versus concentration for monthly exposed lead peroxide cylinders at various locations near Balzac, Alberta (taken from Krouse 1980). The histograms to the right of the diagram give the frequency distribution of $\delta^{34}\text{S}$ values in 2‰ intervals, independent of concentration. Note that the most frequently encountered values correspond to the convergent value at high concentrations. This indicates a dominant emitter with a $\delta^{34}\text{S}$ value near +17‰.

It is well known that the $\delta^{34}\text{S}$ value of seawater SO_4^{2-} is about $+21\text{‰}$. However, lower values are found for marine aerosols.

The superficial layer of about $30\text{ }\mu\text{m}$ thickness at the air/sea interface is highly enriched in organic matter and associated elements such as I, P, and certain heavy metals (McIntyre and Winchester 1969; MacIntyre 1970; Chesselet et al. 1972; Duce et al. 1975; and Morelli 1978).

It has been estimated that the sea produces between 103 and 104 Tg y^{-1} of atmospheric sea salt particles with radii less than $20\text{ }\mu\text{m}$ (Eriksson 1959, 1960; Blanchard 1963; and Petrenchuk 1980). Most of the atmospheric sea salt particles in this size range are produced by whitecap bubbles (Duce 1981). When a bubble bursts at the sea/air interface, atmospheric particles are produced both from the microlayer and from the subsurface seawater. Bonsang et al. (1980) have found that the $\text{SO}_4^{2-}/\text{Na}$ ratio of marine aerosols is always higher than that of seawater (0.25) and can reach 1.25. Moreover, they have shown that the marine aerosols with radii less than $1.1\text{ }\mu\text{m}$ are enriched in SO_4^{2-} from oxidation of organic sulphides released by biological activity at the sea surface. This secondary SO_4^{2-} may be depleted in ^{34}S depending on the origin of the organic sulphides. Data from a number of studies show that the $\delta^{34}\text{S}$ values of SO_4^{2-} in marine aerosols range from -10 to 15‰ . In two studies where gaseous S was also measured, it was on the average depleted by 8 to 10‰ in ^{34}S compared to SO_4^{2-} . Therefore, the isotope data provide evidence that the SO_4^{2-} in marine aerosols has lower $\delta^{34}\text{S}$ values than 21‰ because of the contributions of oxidized biogenic sulphide.

During dissimilatory SO_4^{2-} reduction by strict anaerobes such as Desulphovibrio desulphuricans and Desulphotomaculum, copious dissolved sulphide species are produced in either anoxic waters or sediments. Intense emissions of H_2S to the atmosphere occur in oceanic littorals, lagoons, salt marshes, rice fields, springs, and wet tropical forest soils (Delmas and Servant 1983). In general, isotope fractionation during SO_4^{2-} reduction favours the lighter isotope in the product sulphide. Investigators have found that the $\delta^{34}\text{S}$ value of the sulphide varies from 0 to -70‰ with respect to the substrate sulphate (Deevey et al. 1963; Kaplan and Rittenberg 1964; Nakai and Jensen 1964; Kemp and Thode 1968; Goldhaber and Kaplan 1974; Ivanov et al. 1977; and Weyer et al. 1979).

The isotope fractionation associated with the production of gaseous organic sulphides is more difficult to assess. If they arise from the decomposition of organic S-compounds, the isotopic selectivity should be minimal because a given mass of organic debris should eventually totally decay. Because the isotopic selectivity during SO_4^{2-} assimilation is small, these organic sulphides should be isotopically similar to the original SO_4^{2-} . Another possibility is that gaseous organic sulphides are generated during SO_4^{2-} reduction. This alternative is not well understood.

In the open ocean, the phytoplanktonic and zooplanktonic species principally living in the euphotic layer assimilate sea water SO_4^{2-} and generate sulphides such as CH_3SCH_3 (DMS), CH_3SSCH_3 (DMDS), CH_3SH , and H_2S (Lovelock et al. 1972; Maroulis et al. 1977; Nguyen et al. 1978; Barnard et al. 1982; and Andreae and Raemdonck 1983). These sulphides are released from the water into the atmosphere and are oxidized to SO_2 and ultimately to SO_4^{2-} . Nguyen et al. (1974, 1983) have observed open ocean atmospheric

concentrations of $0.2 \mu\text{g}/\text{m}^3$ for SO_2 and sulphate, respectively, in the sub-Antarctic and Antarctic regions.

For natural samples, it is difficult to delineate biogenic sulphide due to the decomposition of assimilated sulphur from that generated by dissimilatory SO_4^{2-} reduction. The laboratory experiments of Nguyen and Cortecci (1984) may be relevant to this question. The SO_2 generated above algae under restricted air flow had a $\delta^{34}\text{S}$ value of -14.9°‰ which was considerably lower than the value of -3.8°‰ observed in situ.

The oceanic influence on atmospheric S-compounds should decrease at locations further inland. Saltzman et al. (1983) examined atmospheric SO_2 and SO_4^{2-} at the Hubbard Brook Experimental Forest Station, New Hampshire. The $\delta^{34}\text{S}$ values of SO_2 and aerosol SO_4^{2-} were found to range from -1.1 to $+2.3^\circ\text{‰}$ (11 samples) and from $+0.8$ to 3.5°‰ (14 samples), respectively.

Grey and Jensen (1972) found that $\delta^{34}\text{S}$ values from biogenic H_2S at the margins of Great Salt Lake, Utah ranged from 0.0 to $+10^\circ\text{‰}$. Since the maximum value is close to that of SO_4^{2-} in the lake, it might correspond to H_2S generated during plant decay. This would be consistent with the lower SO_4^{2-} reduction activity found in very saline waters.

Biogenic H_2S from cold and warm springs appears to arise almost entirely from SO_4^{2-} reduction because of its significant depletion in ^{34}S . For example, springs near Paige Mountain, NWT, Canada, have SO_4^{2-} with a $\delta^{34}\text{S}$ value near $+20^\circ\text{‰}$. In contrast, the intense biogenic emissions contain H_2S and SO_2 with $\delta^{34}\text{S}$ values of -32 and -38°‰ , respectively. Aerosol H_2SO_4 is similarly depleted in ^{34}S (Krouse and van Everdingen 1984) (Section 4.2.3).

The isotopically selective generation of gaseous reduced S-compounds is not unique to bacteria. Living vascular plants under severe S-stress emit H_2S which is depleted in ^{34}S in comparison to the foliar-S (Section 4.4.7).

Whereas the isotope composition of individual volcanic gases and particulates may vary widely at a given site, the weighted average for $\delta^{34}\text{S}$ of total sulphur tends to be near 0°‰ and has a much smaller spread.

Volcanic activity influences the sulphur isotopic ratio of aerosols in the stratosphere. Castleman et al. (1974) found that after the eruption of Agung, Indonesia, the $\delta^{34}\text{S}$ value increased to $+16$ and then decreased to -24°‰ in stratospheric sulphate. There was also a much smaller decline to about -10°‰ after the eruption of Fernandina in the Galapagos. After several more years without another major eruption, the $\delta^{34}\text{S}$ values showed a tendency to return to small positive values of $+2.6 \pm 0.3^\circ\text{‰}$.

The roasting of magmatic sulphide ores introduces SO_2 which has an average $\delta^{34}\text{S}$ value of about $+2^\circ\text{‰}$ into the atmosphere. Ores from other metal sulphide deposits vary quite widely in their sulphur isotope composition (Section 2.1).

Fossil fuels also range widely in their sulphur isotope composition (Section 2.4). Of particular relevance to the Province of Alberta are emissions from the sour gas industry which range in $\delta^{34}\text{S}$ value from about $+15$ to $+30^\circ\text{‰}$. This is reflected in the isotopic composition of SO_2 near sour gas processing plants (Figure 10).



Figure 10. $\delta^{34}\text{S}$ values for SO_2 collected by lead peroxide exposure cylinders near industrial operations in Alberta, Canada, 1972.

4.2 WATER

4.2.1 Introduction

As seen in Sections 4.1.6 and 4.1.7, the sources of SO_4^{2-} in precipitation are numerous and would be difficult to delineate without the support of S and O isotope data. Upon entering the ground, the complexity is compounded by interactions with different sulphur components in the soil and subsurface minerals. Bacterial SO_4^{2-} reduction further complicates matters in anaerobic environments.

In streams, sulphur removal and acquisition from several sources might occur over many kilometres. Lateral mixing may also be slow (Section 4.2.4).

4.2.2 Groundwater

Factors which control the sulphur and oxygen isotope geochemistry of groundwater may be identified with the recharge environment. These include climate, sources of sulphur, the chemical composition and pH of precipitation, the nature of dry fallout, the role of vegetation, physical and chemical properties of the soil and bedrock, and behaviour of the water table. Chemical reactions and dissolution within aquifers in some circumstances may dominate the groundwater system so that atmospheric inputs in the recharge areas cannot be detected. Nevertheless, isotope data may provide information on the flow patterns which may prove useful for assessing future anthropogenic activities such as fertilizer practices in agriculture and subsurface waste disposal.

In many parts of the world, atmospheric sulphur represents the bulk of the sulphur input to surface waters and shallow groundwater systems. This is particularly true of areas containing sulphur-poor rocks. In isolated regions, the inputs comprise mainly seawater sulphate and biogenic emissions. In other areas, industrial sulphur may dominate, e.g., nickel smelting operations at Sudbury, Ontario.

In some cases, weathering may occur to several metres of depth as in glacial tills in southern Alberta. In this environment, the weathering of organic matter, particularly disseminated coal, is believed to be a substantial source of sulphur. Oxidation and reduction, which will be discussed in more detail in the next section, can in principle set up isotopic gradients with depth. An example is shown in Figure 11. The scenario envisaged is as follows: At a given level of the water table, bacterial reduction occurs in deeper anaerobic zones. The sulphide product precipitates as FeS_2 or other forms. If the water level lowers, unreacted SO_4^{2-} enriched in ^{34}S due to kinetic isotope effects during the reduction (Section 2.2) migrates downwards. The sulphide minerals, depleted in ^{34}S , are exposed to oxidation. Waters flowing downwards from the surface may also contain SO_4^{2-} not as enriched in ^{34}S as that in the older, deeper water. Repeated vertical cycling over thousands of years could set up distributions similar to those shown in Figure 11. It must be pointed out, however, that there are some complications with this interpretation for the glacial tills (J. Hendry, personal communication). Impermeable layers exist in the stratigraphic column and there is concern that, to some extent, H_2S production in these wells may have been enhanced by the drilling operations. If the latter is true, this would not detract from the value of the stable isotope data since they would be reflecting the consequence of an anthropogenic activity.

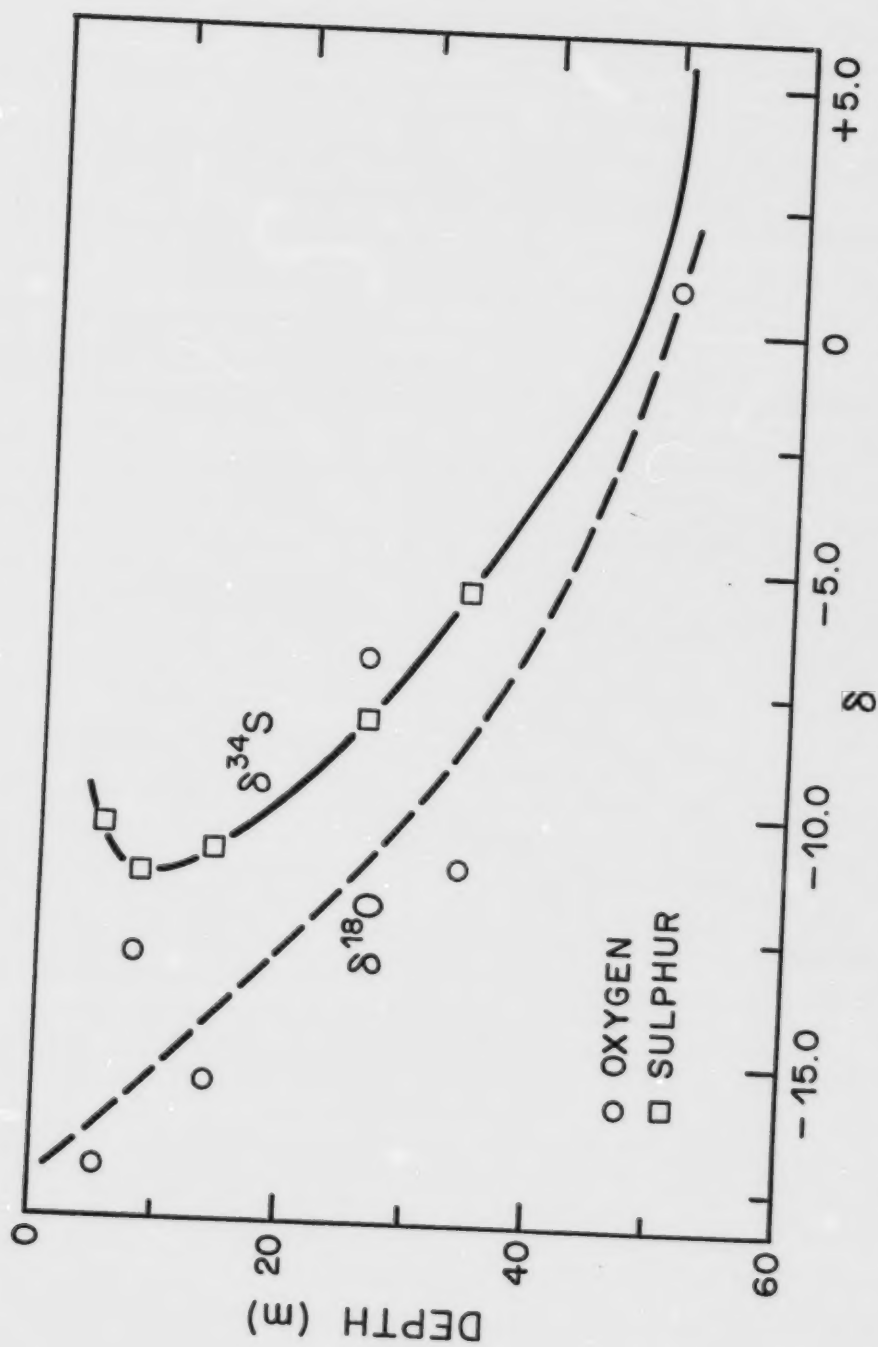


Figure 11. Trends in $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of SO_4^{2-} with depth in glacial tills of southern Alberta (Shakur 1982).

The oxidation of organic sulphur and pyrite in the unsaturated zone of coal spoil piles at Battle River, Alberta was investigated isotopically by Wallick and Huenmert (1983). Lower $\delta^{34}\text{S}$ values were found in shallower waters and the scenario of redox cycles described above is credited with the migration of ^{34}S enriched SO_4^{2-} downward to the water table.

In the course of SO_4^{2-} reduction, unreacted SO_4^{2-} becomes enriched in ^{18}O as well as ^{34}S . During oxidation, however, oxygen is introduced to the SO_4^{2-} from H_2O which is very depleted in ^{18}O . Thus, the vertical distribution in $\delta^{18}\text{O}$ in Figure 11 is also consistent with the redox cycles attending changes in the level of the water table.

An example of using S isotopes for identifying flowpaths in connection with a nuclear waste disposal program at the Asse Saltdome in Germany has been described by Frank (1974). In this case, several evaporite occurrences of different geological ages were involved. Hence the curve for secular variations in the $\delta^{34}\text{S}$ values of marine SO_4^{2-} (Section 2.1) was used to chart the strata through which the waters migrated.

Weyer et al. (1979) carried out a regional geohydrological isotope investigation in northwestern Canada which extended a distance of over 200 km from the Caribou Mountains plateau (elevation 1000 m) northward to the south shore of Great Slave Lake (elevation 156 m), and about 200 km from Hay River in the west to Little Buffalo River and Slave River in the east. The Caribou Mountains consist mainly of clastic Cretaceous rocks and the associated waters had $\delta^{34}\text{S}$ values for SO_4^{2-} of -10‰ and lower. The surrounding lowlands have many outcrops of Upper and Middle Devonian calcareous gypsiferous and evaporitic rocks with $\delta^{34}\text{S}$ values near $+20\text{‰}$. The numerous Pine Point Pb-Zn sulphide deposits on the south shore of Great Slave Lake also have $\delta^{34}\text{S}$ values near $+20\text{‰}$.

Samples were measured in surface waters, wells, springs, and boreholes. In most cases both dissolved sulphide and sulphate were examined. The difference in $\delta^{34}\text{S}$ values for these two ions was as large as 70‰ whereas the most frequently encountered difference was 40‰ . Under such conditions, it was necessary to know the sulphate and sulphide concentrations to calculate the mean $\delta^{34}\text{S}$ values in order to identify different sources. After this exercise, the number of possible sources was reduced to four with $\delta^{34}\text{S}$ values of -10 , 0 , $+10$, and $+18\text{‰}$. The two extreme values could be related to Cretaceous and Devonian rocks, respectively. Identification of the remainder is more difficult although there is some evidence that the $+10\text{‰}$ may also be an evaporitic source.

In the above study, hydrogen isotope data were also found to be useful for characterizing different water groups. A group with a given δD range might be further separated on the basis of a chemical parameter such as $[\text{Cl}^-]/[\text{SO}_4^{2-}]$ ratios or vice-versa. Thus, the authors could answer questions such as whether a given spring might be hydrologically connected to a nearby river.

Rightmire et al. (1974) examined SO_4^{2-} in the Floridan aquifer. The $\delta^{34}\text{S}$ values did not show a systematic variation with the flow pattern although the lowest values were found in the major recharge area. They concluded that three sources were involved: ocean water, rainfall, and solution of gypsum. They found the difference in $\delta^{34}\text{S}$ values between SO_4^{2-} and H_2S to be fairly consistent near 60‰ and interpreted this to possibly reflect the approach to isotopic equilibrium exchange conditions between the two species. The bulk of the opinion would hold that this equilibration is unlikely at such

low temperatures. However, the possibility that a biochemical mechanism might promote the exchange during bacterial SO_4^{2-} reduction should not be dismissed.

4.2.3 Springs (With Emphasis on Western Canada)

Sulphur isotope variations in springs throughout the world were reviewed by Krouse (1974). They were classified into a number of categories. Springs with $\delta^{34}\text{S}$ values near 0‰ for both SO_4^{2-} and HS^- were considered as bearing primary or magmatic sulphur. Some of the springs in Yellowstone Park fit this category (Schoen and Rye 1970). It should be emphasized that springs in geothermal areas may not always bear magmatic sulphur. Indeed some volcanic systems may pump seawater through rock fractures. Another category includes springs bearing recent seawater sulphate. Possible candidates are Kyuquot Sound, Vancouver Island, Canada, and Milk River Bath in Jamaica.

Sulphur in springs is probably most frequently derived from dissolution of sediments. In rarer cases, sulphides are oxidized to form colourful deposits such as natro-jarosite limonite and goethite (Paint Pots, Kootenay National Park, British Columbia), as well as barite sinters. Sulphate in such springs is often depleted in ^{34}S and always depleted in ^{18}O (Shakur 1982; Cecile et al. 1983; and van Everdingen et al. 1985), attesting to solution of sulphide minerals and incorporation of oxygen in the SO_4^{2-} from ^{18}O -depleted waters during oxidation.

The bulk of the springs in western Canada are depositors of travertine with sulphate derived from marine evaporites as revealed by the sulphur and oxygen isotope composition of the SO_4^{2-} (Krouse et al. 1970; Krouse 1974; and van Everdingen et al. 1982, 1985) (Figure 12).

The depletions of ^{34}S in HS^- relative to SO_4^{2-} is the consequence of the action of SO_4^{2-} -reducing bacteria. Such bacteria have been isolated from these springs and their ability to fractionate sulphur isotopes studied in the laboratory (Smejkal et al. 1971). Elemental sulphur and secondary sulphate are also depleted in ^{34}S if they are the product of sulphide oxidation.

In the case of springs near Paige Mountain, Norman Range, NWI, oxygen isotope analyses of SO_4^{2-} proved capable of interpreting aspects of sulphur geochemistry not discernible with sulphur isotopes. During subsurface flow, a significant percentage of the SO_4^{2-} had been reduced and reoxidized. Sulphur isotopes were conserved so that they provided no evidence of the phenomenon. On the other hand, the $\delta^{18}\text{O}$ values of SO_4^{2-} had been shifted downwards from that of the anhydrite source, attesting to incorporation of oxygen from the water during the reoxidation.

In the above study, the fate of the biogenic H_2S emissions was also documented by isotopic analyses of atmospheric SO_2 , H_2SO_4 , and secondary sulphates formed on the surrounding terrain. Large $\delta^{34}\text{S}$ variations in soil and vegetation were also recorded in the vicinity, dependent upon the relative uptake of primary SO_4^{2-} or atmospheric sulphur oxides generated from the biogenic H_2S (Krouse and van Everdingen 1984).

A study similar to that for Paige Mountain was conducted at the Cave-and-Basin site, Banff, Alberta (van Everdingen et al. 1985). This study implicated corrosion by fallout H_2SO_4 (oxidation product of biogenic H_2S emissions) in the formation of the cave. The sulphur and oxygen isotope systematics are shown in Figure 13.

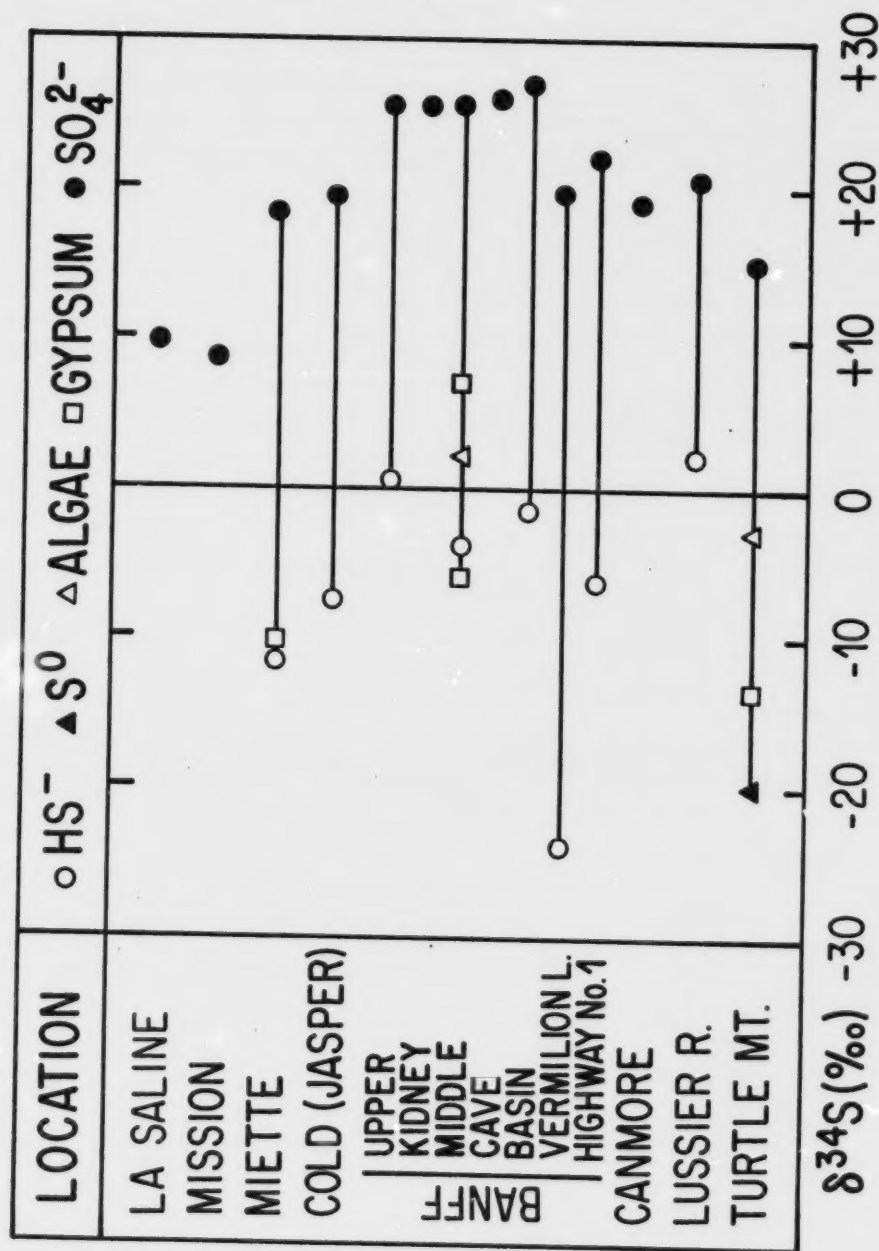


Figure 12. $\delta^{34}\text{S}$ variations in springs of Alberta where SO_4^{2-} is derived by dissolution of evaporites.

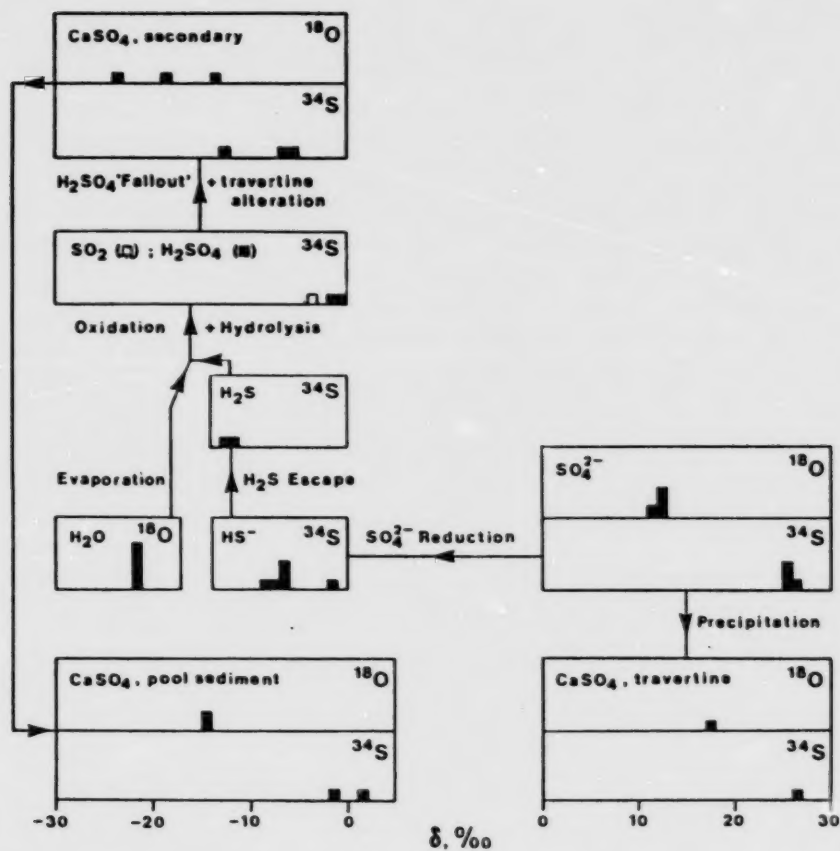


Figure 13. Histograms of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values for sulphur species at the Cave-and-Basin, Banff, Alberta (taken from van Everdingen et al. 1985). Evidently corrosion by atmospheric H_2SO_4 from the oxidation of biogenic H_2S has played a significant role in forming the cave.

4.2.4 Rivers and Streams

A number of sulphur isotope studies have been described for river systems (Veselovsky et al. 1969; Longinelli and Cortecci 1970; Hitchon and Krouse 1972; Holt et al. 1972; and Chukhrov et al. 1975). Longinelli and Cortecci (1970) measured both the sulphur and oxygen isotopic content of sulphate in two rivers in Tuscany. They noted that SO_4^{2-} was progressively enriched in both ^{34}S and ^{18}O sulphate from the head waters toward the outlet of the river systems. In the upper reaches of both rivers, the sulphate concentration was less than 10 mg/L and the $\delta^{34}\text{S}$ values ranged from -3 in one system to -12‰ in the other. $\delta^{18}\text{O}$ values of the sulphate varied from 0 to $+4\text{‰}$. Near the points of discharge of the rivers to the ocean, the sulphate concentration was considerably higher and the $\delta^{34}\text{S}$ values were in the range of +3 to $+12\text{‰}$. This is still less than normal oceanic sulphate which is about $+20\text{‰}$. The ^{18}O content of the sulphate, however, was in the range expected of oxygen in oceanic sulphate, being in the range of +6 to $+11\text{‰}$. Longinelli and Cortecci were unable to correlate the changes they found in these rivers with the geology of the regions.

Hitchon and Krouse (1972) reported a number of analyses from rivers and streams in the Mackenzie River system of northwestern Canada. They found a range of $\delta^{34}\text{S}$ values for sulphate from -20 to $+20\text{‰}$. On the basis of chemical and factor analyses they deduced a rough but clear relationship between the isotopic composition of the river sulphate and the geology of the basin (Figure 14). In particular, in basins draining Paleozoic rocks known to contain evaporites at depth, all the $\delta^{34}\text{S}$ values were positive. On the other hand, streams draining basins underlain by marine Cretaceous rock had negative $\delta^{34}\text{S}$ values. In these basins it is probable that the sulphate is derived from the oxidation of pyrite or perhaps organic S. Cretaceous shale outcrops are encountered in the Peace River region and soils there have very negative $\delta^{34}\text{S}$ values consistent with the river data.

Chukhrov et al. (1975) found systematic relationships between the geology of the basins and the $\delta^{34}\text{S}$ values of sulphate in assorted rivers throughout the USSR. For example, the upper reaches of the Kuma River receive water from Cretaceous and Jurassic rocks containing evaporitic sulphate minerals. $\delta^{34}\text{S}$ values of the sulphate in this portion of the river range from +8 to $+14\text{‰}$. Further downstream, this river receives sulphate which is probably derived from pyrite in the basin, and the $\delta^{34}\text{S}$ of the river SO_4^{2-} decreases to -5‰ .

Very few studies have examined streams in cross-section. This is unfortunate because, for example, Krouse and Mackay (1971) showed with oxygen isotopes that the Mackenzie and Liard Rivers required a distance of nearly 400 km for thorough lateral mixing. An appreciation of the slow mixing of flowing water is also illustrated by the data for a cross-section of the City of Calgary river system depicted in Figure 15. Both concentration and $\delta^{34}\text{S}$ values fluctuate in the main stream. The east branch stream is particularly interesting because of the higher SO_4^{2-} concentration and much lower $\delta^{34}\text{S}$ value in comparison to the main stream. These factors pinpoint a source to the east or north of the east branch since contributions from further upstream should have altered sample 6 in the main stream. These data suggest that the slow rate of lateral mixing may permit the identification of several sources of pollutants in some streams on the basis of isotopic analyses of a cross-section.

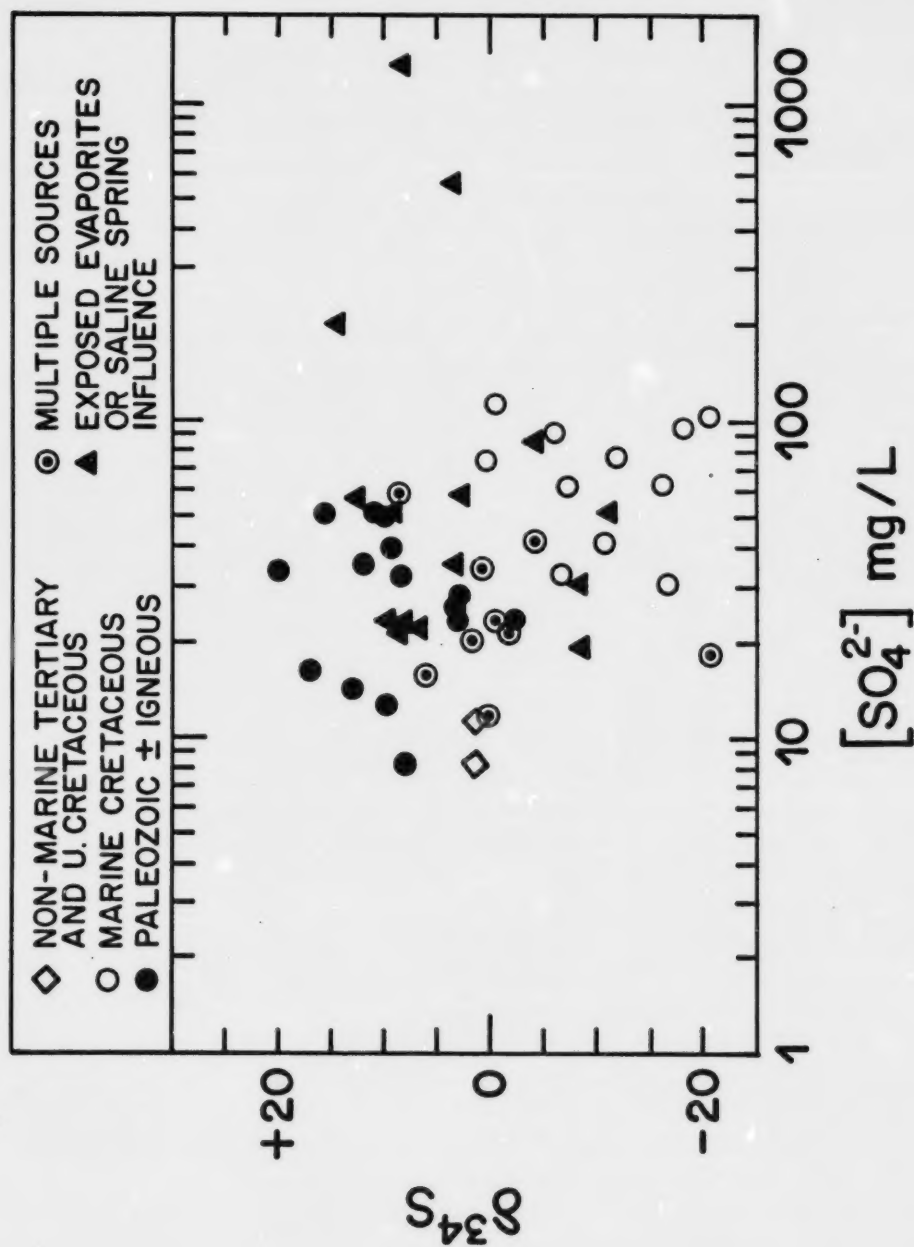


Figure 14. $\delta^{34}\text{S}$ versus concentration for SO_4^{2-} in the Mackenzie River system in relation to the basin geology (data from Hitchon and Krouse 1972).

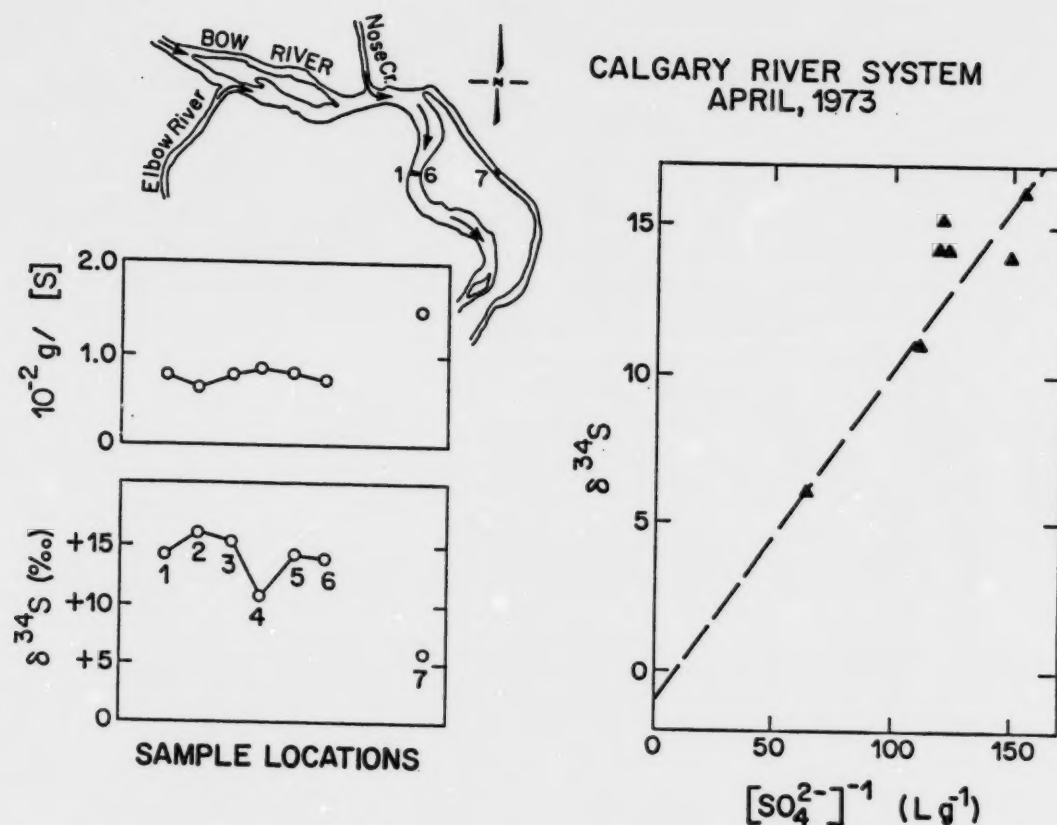


Figure 15. Sulphur isotope variations in aqueous sulphate in a cross-section of the Bow River, City of Calgary, April 1973. Sample 7 in the side stream has a higher sulphate concentration and a much lower δ -value than samples in the mainstream and identifies a source just north of the sampling site. A plot of $\delta^{34}\text{S}$ versus $[\text{SO}_4^{2-}]^{-1}$ extrapolates to a $\delta^{34}\text{S}$ value of -10‰ for this source. Scatter about the line plot is related to non-mixing and perhaps biological conversions (taken from Krouse 1980).

4.2.5 Lakes and Ponds

The sulphur isotope composition of SO_4^{2-} in a pond or lake depends upon the stream and groundwater inputs and geochemical processes within the water body and its sediments.

The sediments may exercise considerable control on the concentration and isotopic composition of the SO_4^{2-} . One process which may be of importance is physical adsorption of sulphate. In experiments with organic-rich sediments (11.5% organic C) from the Bay of Quinte, Lake Ontario, Nriagu (1974) found SO_4^{2-} in solution to change in $\delta^{34}\text{S}$ value from 0.9 to +6.0‰, implying that ^{32}S was preferentially adsorbed by the sediments. Assuming no losses by other processes, the difference in isotopic composition between SO_4^{2-} in solution and that adsorbed ranged from 10 to 24‰ in these experiments. Thus, adsorption in the sediments can in principle decrease the $\delta^{34}\text{S}$ values of freshwater bodies.

Another significant process which occurs in the sediments is bacterial SO_4^{2-} reduction. It appears that in many cases, the sulphur isotope fractionation may be minimal in that the input of SO_4^{2-} , rather than SO_4^{2-} reduction, may be rate-controlling, i.e., the isotopic selectivity of the latter is not expressed. It is interesting that in studies of lake cores, there may be marked shifts towards negative $\delta^{34}\text{S}$ values in the upper 4 or 5 cm. This has been noted in lakes of Northern Ontario (Nriagu and Coker 1983) and New York (M. Mitchell and H.R. Krouse, unpublished data). The dilemma is that the industrial sulphur that should reside in the upper layers does not have such negative $\delta^{34}\text{S}$ values. One explanation is that the influx of pollutant S exceeds the rate of SO_4^{2-} reduction. Hence, the sulphur fixed in the upper sediment is depleted in ^{34}S because of the kinetic isotope effects during reduction.

Although bacterial SO_4^{2-} reduction tends to be maximal just below the water/sediment interface, it may occur extensively in the water column. This is particularly true of ice covered, stratified lakes in the Antarctic (Nakai et al. 1975) and Ellesmere Island in the Canadian Arctic (Jeffries et al. 1984). The bottom waters of these lakes are modified seawater that was trapped in a fiord situation a few thousand years ago. The ice cover of about 2m prevents vertical mixing. As a consequence of bacterial reduction, in some cases, unreacted SO_4^{2-} has $\delta^{34}\text{S}$ values higher than +100‰.

Smaller scale systems of large sulphur isotope fractionations during bacterial SO_4^{2-} reduction under ice cover are found in Alberta. One example is the City of Camrose water-sewer system (Figure 16). For simplicity of discussion, consider the No. 5 Lagoon. In the winter, when waters are ice covered, oxygen for sewage oxidation tends to be derived from inorganic ions such as SO_4^{2-} . Consequently, copious quantities of aqueous sulphide ions with large depletions of ^{34}S (-55‰) formed and the unreacted SO_4^{2-} became isotopically heavier. When breaks occurred in the ice cover, aerobic bacteria which utilized atmospheric oxygen became more active in processing the sewage. Under these conditions, some of the sulphide formed by the SO_4^{2-} reducers was probably reoxidized. Hence, the net sulphide production decreased and the sulphate and sulphide isotopic composition tended to become isotopically lighter and heavier, respectively, as spring approached. The changing temperature in all likelihood altered the isotopic selectivity of the SO_4^{2-} reducers so that the situation cannot be described in terms of a constant kinetic isotope effect.

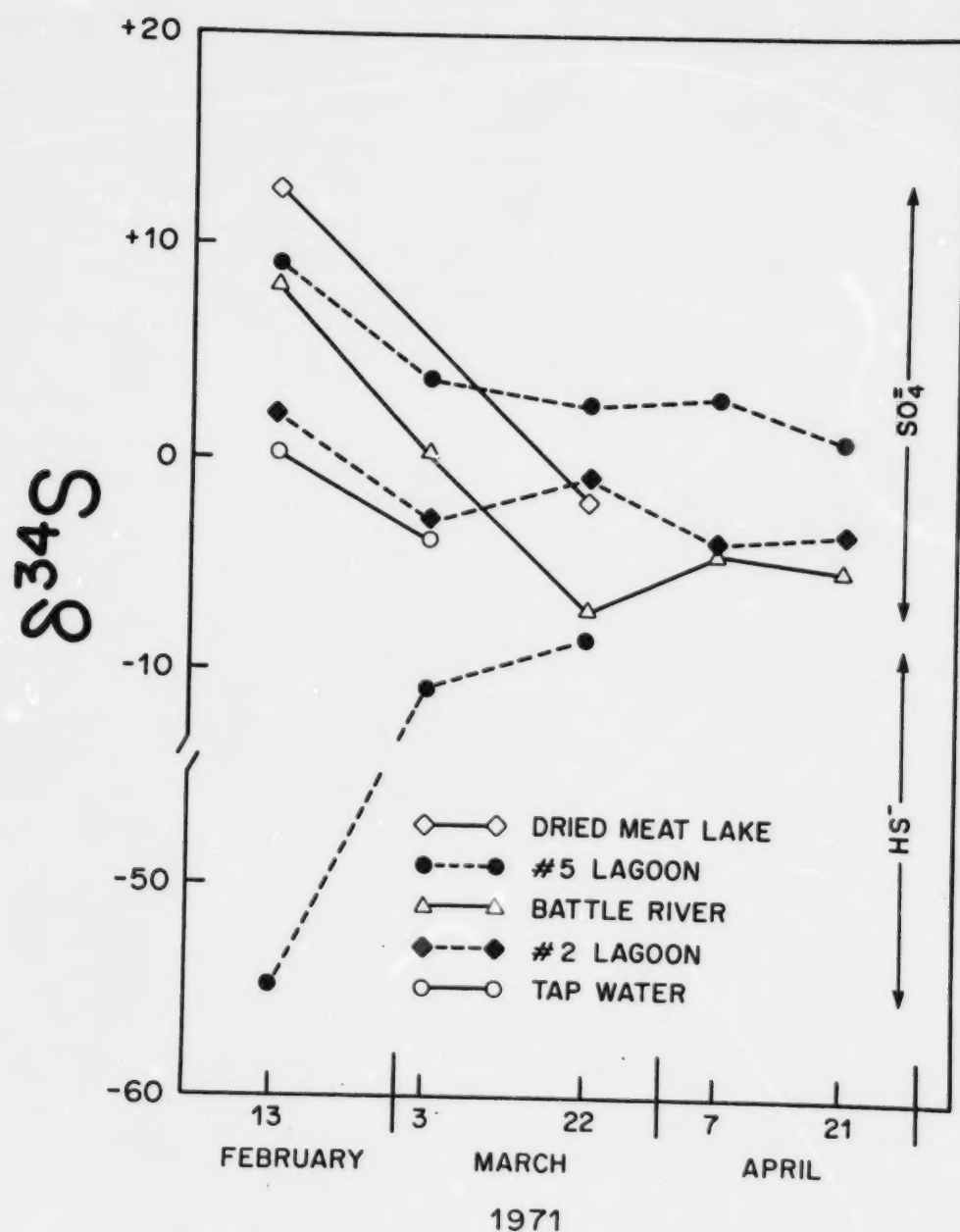


Figure 16. Isotopic behaviour of sulphur compounds in the Camrose, Alberta sewer system. When the lagoons are ice covered, anaerobic sulphate-reducing bacteria are more active and produce H_2S greatly depleted in $\delta^{34}S$. When the ice breaks up, most of this sulphide is reoxidized and aerobic bacteria become more prevalent (taken from Krouse 1980).

Copious H_2S may be generated under ice cover in liquid manure installations. This, on occasion, has proved fatal for farm workers in Alberta. There are two possible modes of H_2S production: degradation of organo-sulphur compounds and bacterial reduction of SO_4^{2-} in the groundwater. The latter is the chief cause (F.D. Cook, personal communication, 1971).

Sulphur isotope data have been used to establish the presence of sulphur from smelting operations in lakes of Northern Ontario (Nriagu and Harvey 1978). The $\delta^{34}\text{S}$ values of ores being smelted may range from 0 to 7‰. Within 10 km of the Sudbury stack, the $\delta^{34}\text{S}$ values varied from +2 to +8‰, whereas beyond that distance, they were more uniform, around +5‰. It is noted that many of these lakes on the Canadian Shield are poorly buffered and the atmospheric S constitutes the major input.

In the case of sour gas processing operations in Alberta, industrial S may enter surface waters from the atmosphere or by oxidation of elemental S either as dustfall or in soil near storage blocks. Sulphur isotopes readily document the extent of industrial S (Figure 17).

An important question is the extent to which sulphur of industrial origin might interact with organic matter in the environment. Evidence of such interaction is provided by data from surface waters in the West Whitecourt study area (Figure 17). It is seen that the $\delta^{34}\text{S}$ values increase sympathetically with the concentrations of dissolved organic sulphur compounds and asymptotically approach the value of the industrial S. Therefore, one concludes that industrial S in the hydrosphere increased the $\delta^{34}\text{S}$ value of SO_4^{2-} and reacted biologically or abiologically with organic matter.

4.3 SOIL

4.3.1 Sources of Sulphur Compounds in Soil

The pedosphere is the site of many complex interactions between the lithosphere, biosphere, atmosphere, and hydrosphere. In terms of the sulphur cycle, the major inputs are organic matter, dry and wet deposition of atmospheric sulphur compounds, groundwater leaching of subsurface minerals, and in cultivated regions, fertilizer applications. The main outputs are leaching into groundwater and river runoff, and biogenic emissions of gaseous sulphur compounds.

The sources of sulphur compounds in the soil embrace not only inputs from the atmosphere, biosphere, and lithosphere via the hydro-sphere, but also transformations within the soil. Solution SO_4^{2-} constitutes the central pool in Figure 18. It can flow to the microbial S pool, plants, and various inorganic forms. Foliar sulphur returns to the soil either directly (e.g., falling leaves) or indirectly by grazing animals. Volatile sulphide compounds are lost to the atmosphere but they can in turn be oxidized to SO_2 . The SO_2 can return to the ground intact (dry fall) or be oxidized to SO_4^{2-} which returns to the soil in precipitation.

Anthropogenic sulphur can enter soil by many of the pathways shown in Figure 18. When a given flux is augmented by pollutant S, other fluxes tend to adjust accordingly. For example, SO_4^{2-} added to soil is rapidly converted to organic sulphur. Consequently, concentration determinations of soil SO_4^{2-} cannot provide an accurate assessment of uptake of pollutant sulphate from the atmosphere. However, if the isotopic

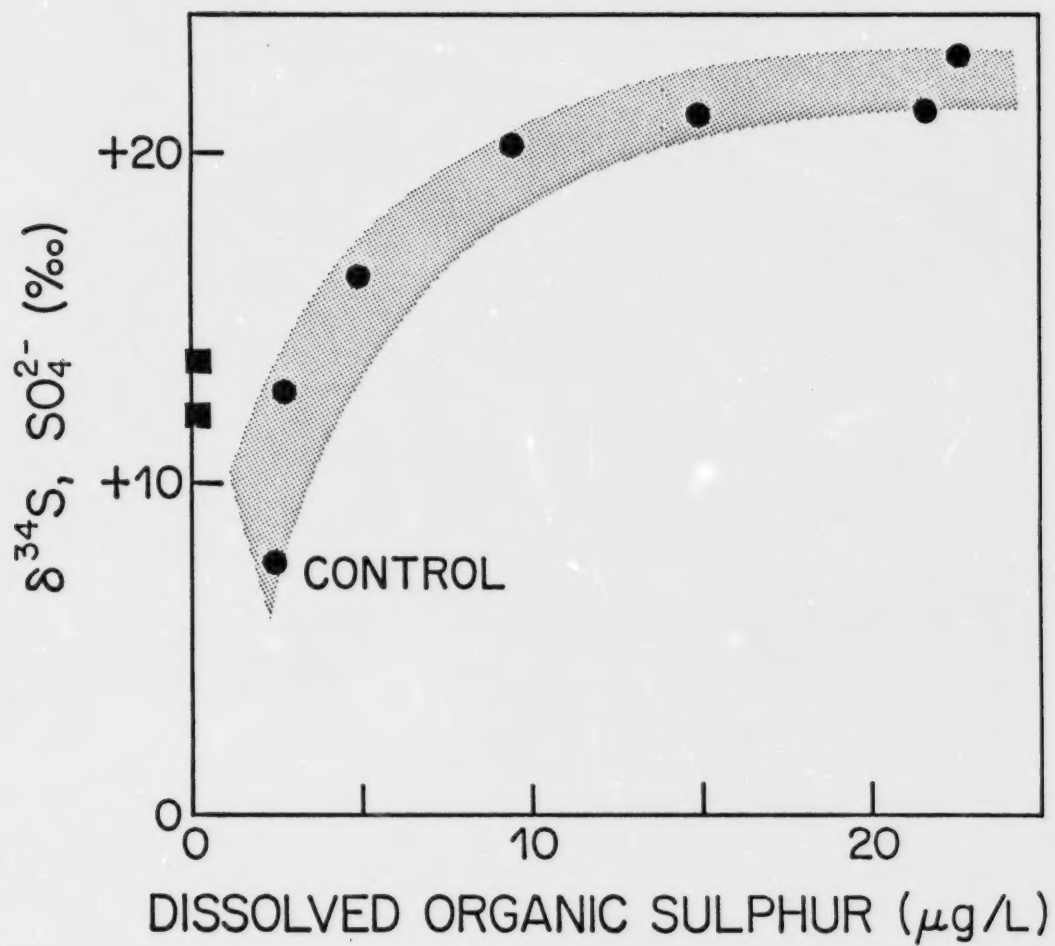


Figure 17. $\delta^{34}\text{S}$ values for SO_4^{2-} versus dissolved organic sulphur content, West Whitecourt study area (Krouse et al. 1984). The sympathetic increase in $\delta^{34}\text{S}$ with organic S content reflects industrial S enriched in ^{34}S reacting with organic compounds.

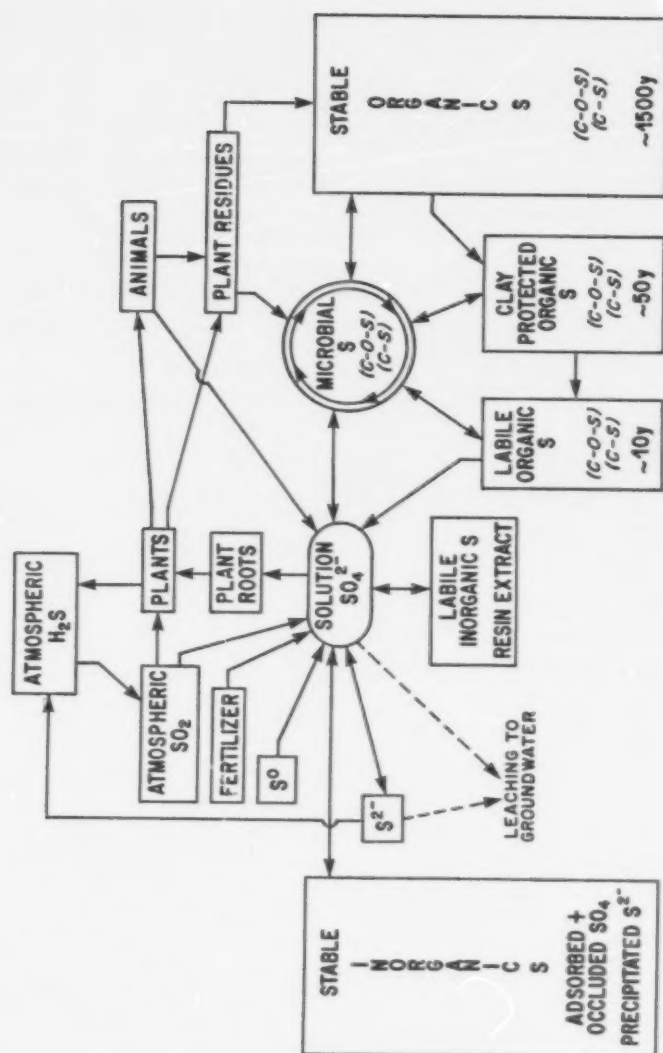


Figure 18. Pools of sulphur compounds in soil (taken from Krouse et al. 1987).

composition of the indigenous sulphate differs from that of the added pollutant sulphate, the $\delta^{34}\text{S}$ value of the mixture is a direct measurement of the relative amounts of each component, even if the SO_4^{2-} pool is depleted by conversion to organic S. The accuracy of the isotopic approach depends upon whether there is isotopic fractionation during the SO_4^{2-} conversions. During assimilation, the isotopic selectivity is usually small, whereas large kinetic isotope effects accompany dissimilatory (respiratory) SO_4^{2-} reduction. Such situations are expected in wetlands. However, many soil situations of interest are aerobic and isotope fractionation during SO_4^{2-} reduction should not present problems.

4.3.2 Sulphur and Oxygen Isotope Variations in Soil

Soils range widely in their $\delta^{34}\text{S}$ values because of isotopic variations in parent materials and sulphur gains from, and losses to the atmosphere, hydrosphere, and biosphere.

A world survey of soil $\delta^{34}\text{S}$ values has not been conducted. In most cases, data were obtained in areas where concerned environmental agencies wished to evaluate the effects of existing industrial pollution. However, there are sufficient data to draw some conclusions regarding sources of sulphur compounds and their transformations (Figure 19).

The large range of $\delta^{34}\text{S}$ values in Figure 19 (from below -30‰ to above $+30\text{‰}$) can be related to a variety of natural and anthropogenic sources of sulphur. For instance, soils from various locations in New Zealand have $\delta^{34}\text{S}$ values approaching those of seawater SO_4^{2-} (Kusakabe et al. 1976). These authors concluded that sea spray was the principal source of soil sulphur even in inland basins with little rainfall. Whereas New Zealand soils appear to derive marine sulphate from modern sea spray, other soils such as the few studied in Tunisia by Kusakabe et al. (1976), derive sulphate from gypsum occurrences related to the ancient ocean.

The data for the USSR in Figure 19 are those casually mentioned in the thorough study of plants in various regions by Chukhrov et al. (1978). There is a considerable range in sulphur isotope composition with many data near $+3\text{‰}$. These authors attributed the wide range in $\delta^{34}\text{S}$ values to essentially three processes which varied with locality. These are: (1) local weathering of rocks with evaporite and sulphide ores representing extreme situations; (2) inputs of sulphate from the atmosphere; and (3) bacterial SO_4^{2-} reduction in less aerobic environments leading to differentiation of $\delta^{34}\text{S}$ values with soil depth.

As in the USSR, data from many other locations in the world fall near 0‰ , which is considered to approximate the terrestrial mean (Figure 19). In some cases, these signify natural sources but in other situations (e.g., Wawa, Ontario; Thompson, Manitoba) smelting of sulphide ores of deep crustal origin is involved.

Soils very depleted in $\delta^{34}\text{S}$ (-30‰) are often encountered (c.f. California and Alberta, Figure 19). Surface or shallow occurrences of Cretaceous shales are found in some of these locations. Therefore, the soil S is believed to be derived from weathering of ^{34}S -depleted sulphide minerals and perhaps organic sulphur in shales.

Organic soils developing under anaerobic reducing conditions may exhibit depletions in $\delta^{34}\text{S}$. An example is a peat deposit in Northern Alberta (Figure 20).

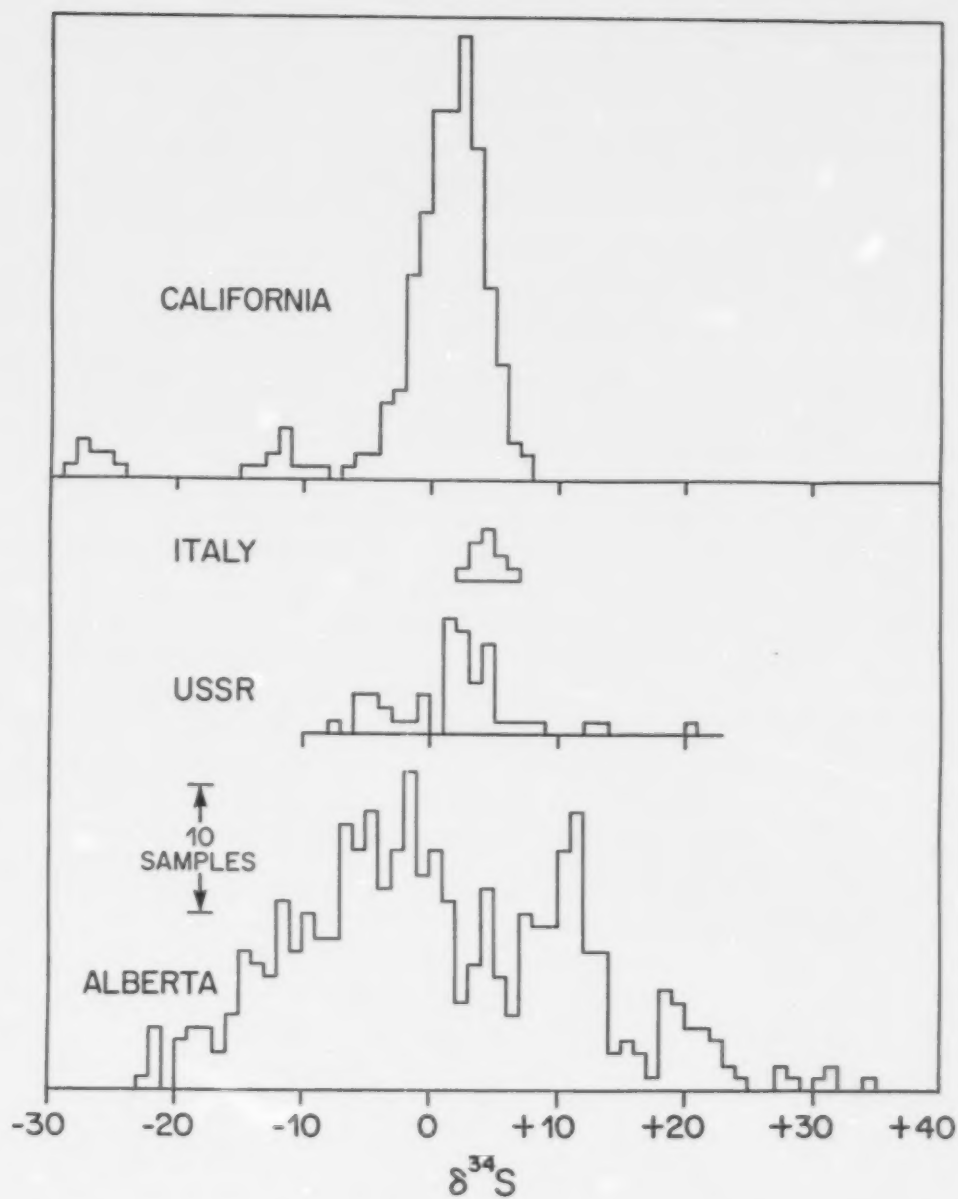


Figure 19. $\delta^{34}\text{S}$ variations in soil, regardless of horizons (taken from Krouse et al. 1987).

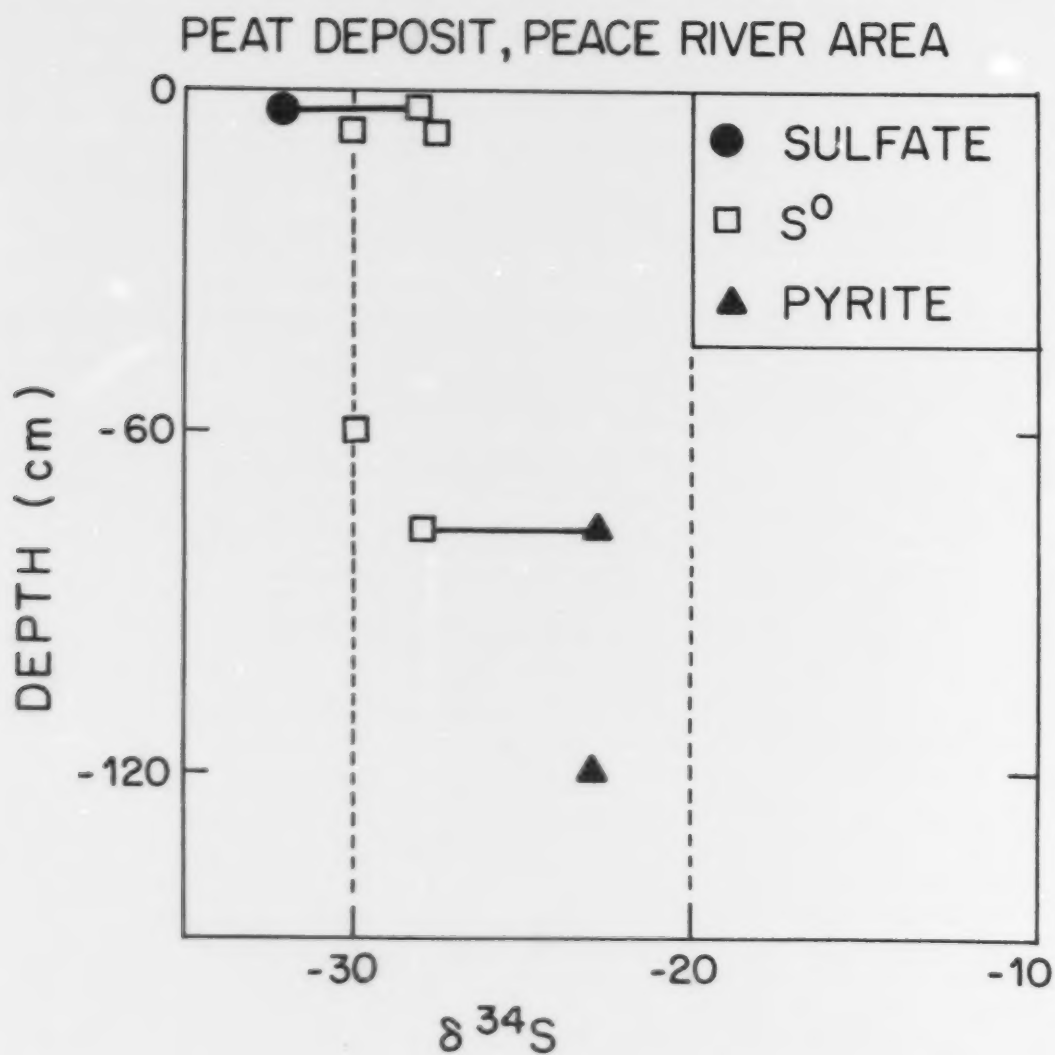


Figure 20. Sulphur isotope data for FeS₂, S⁰, and sulphate in a peat deposit, northern Alberta.

At 1.2 m depth, pyrite was the dominant sulphur species with a $\delta^{34}\text{S}$ value near -24‰ . At 80 cm depth, elemental sulphur was also present with a $\delta^{34}\text{S}$ value near -28‰ . At 50 cm depth, pyrite was absent and elemental sulphur very abundant. On the surface, sulphate salts were present with a $\delta^{34}\text{S}$ value near -33‰ whereas co-existent S^0 had a $\delta^{34}\text{S}$ value near -30‰ . This sulphur isotope pattern is the converse of that identified with thermodynamic equilibrium and is diagnostic of kinetic isotope effects during the oxidation sequence, sulphide $\rightarrow \text{S}^0 \rightarrow$ sulphate; that is, ^{32}S -containing species were oxidized preferentially, yielding products comparatively depleted in ^{34}S .

Quite positive $\delta^{34}\text{S}$ values are found in soils near travertine (CaCO_3 , minor $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) depositing springs, reflecting evaporite strata which were dissolved at depth by these waters (Section 4.2.3). In many locations in Alberta, such positive $\delta^{34}\text{S}$ values in soil are the consequence of emissions from sour gas processing.

Thus, the wide variations in $\delta^{34}\text{S}$ values in soil embrace both natural and anthropogenic sources. Sulphur isotope data in combination with concentration measurements can often be used to delineate those sources.

4.3.3 Relationships Among $\delta^{34}\text{S}$ Values of Different Soil Extracts

$\delta^{34}\text{S}$ variations among different S compounds or compound classes can be attributed to isotope selectivity in biochemical reactions. However, the extracts usually obtained in soil analyses are mixtures of compounds which cannot be readily related to specific biological processes.

In a few studies, $\delta^{34}\text{S}$ values have been reported for water soluble S along with either insoluble or total S. Although the soluble fraction is mainly SO_4^{2-} , some soluble organic S compounds may be included. Since the insoluble S fraction is the remnant of extraction by water or salt solutions, it will contain varying amounts of sulphate inversely related to the soluble S recovery efficiency.

For many locations in Alberta, Canada, the $\delta^{34}\text{S}$ values for total soil S are systematically lower than those for soluble S (Figure 21). It is tempting to attribute this phenomenon to a kinetic isotope effect during conversion of SO_4^{2-} to water insoluble organic S. However, another explanation is more likely. Elevated concentrations of industrial sulphur compounds at these locations are enriched in ^{34}S . Most of the soluble S, particularly in the upper LFH soil horizon, came from the atmosphere. Deciduous leaves contributed significantly to the insoluble organic S content of this soil horizon. While living, these leaves acquired ^{34}S -depleted sulphur from lower soil horizons as well as ^{34}S -enriched S from the atmosphere. Thus, the isotopic difference between the two soil components is readily explainable by two sources with different mixing ratios. Although SO_4^{2-} can be transformed to organic S quickly and the process probably has little attending isotope selectivity, the oxidation of the organic S to SO_4^{2-} would be slower. Therefore, the inorganic and organic S components had probably not been homogenized isotopically.

In contrast, many data for deeper soil horizons in Alberta fall below the line of unity slope. This can be explained by an argument similar to that above except the dominant source of soluble S is a subsurface sulphate mineral source depleted in $\delta^{34}\text{S}$. In the deeper horizons, organic S would have less influence on the SO_4^{2-} pool because of its lower concentration and slower oxidation in more anaerobic conditions.

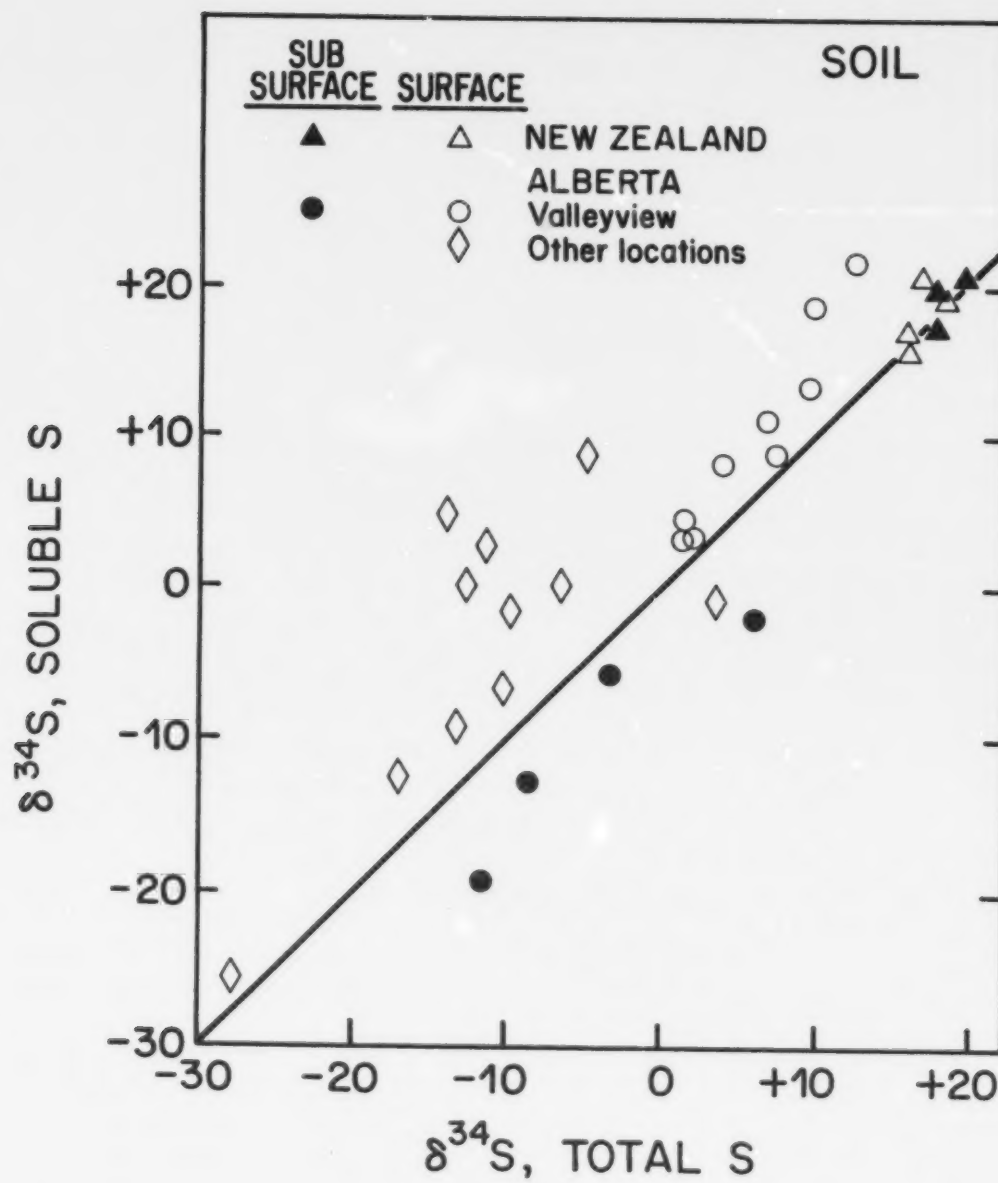


Figure 21. $\delta^{34}\text{S}$ values of soluble S versus those of total S in soil samples (taken from Krouse et al. 1987).

In the New Zealand soils studied by Kusakabe et al. (1976), the data fall close to the line of slope unity, passing through the origin in Figure 21. These authors concluded that there is negligible isotopic selectivity during SO_4^{2-} to organic S transformations and the soil components which they studied were homogeneous in S isotope composition.

Examination of available data suggests that if soil sulphur is derived consistently from one source (e.g., sea spray for New Zealand soils), the water soluble and insoluble organic S fractions acquire similar isotopic compositions. If there are two or more sources or if the isotopic composition of atmospheric or groundwater SO_4^{2-} fluctuates, there may not be sufficient time for isotopic homogenization. Whereas the microbial conversion of SO_4^{2-} to organic S can be rapid, oxidative turnover of the much larger accumulated organic S pool requires more time. Therefore, the latter process would appear to be rate controlling in establishing isotopic uniformity among sulphur pools.

Elemental sulphur may be added to soil as applied fertilizer or atmospheric dust in the vicinity of sulphur block storage and loading operations. Potted soil experiments demonstrate that during chemical and bacterial oxidation of S^0 , the sulphur isotope selectivity is very small (McCready and Krouse 1982) presumably because the reaction occurs primarily on the sulphur surface. Therefore, sulphur isotope analyses of SO_4^{2-} over time can reveal how effectively the S^0 is oxidized, provided that natural sulphates are either low in concentration and/or of quite different isotope composition. During the reaction, oxygen atoms are incorporated from both H_2O and atmospheric O_2 . Therefore, oxygen isotope data for sulphate may also prove useful to delineate natural sulphate from that derived by oxidation of the applied S^0 .

4.3.4 Transfer of Sulphur into the Soil as Revealed by Sulphur Isotope Data

There are a number of pathways by which atmospheric or surface applied sulphur may enter the soil (Figure 18). Of these, the dominant mechanism is leaching of SO_4^{2-} . In acid soils, downward movement will be impeded by sorption of SO_4^{2-} by Al and Fe compounds. Other factors of importance include movement of organic compounds and biological transformations. In heavily wooded damp environments, sulphur of atmospheric origin may be confined to moss and litter layers as illustrated by data from Ram River and Whitecourt in Section 5.

Behaviour of groundwater should be a factor. Downward transport of sulphur compounds should be enhanced in recharge areas whereas in saline areas, SO_4^{2-} may be moved upwards under artesian pressure.

For industrial pollutants, the penetration of atmospheric compounds into the soil will depend upon the rates and duration of the emissions. It will not be simply related to the accumulated fallout. Some atmospheric sulphur reaches the soil via falling leaves. The extent to which the vegetation and organic cover remains intact is also a factor. Thus, SO_2 episodes at high concentration levels for short time intervals could break down the retention capabilities of the surface cover whereas the same total SO_2 with uniform exposure might not prove detrimental.

A controversial concept is that sulphur compounds might penetrate to even the B and C soil horizons by translocation in the plants to the roots. Epstein (1972) stated that sulphate is moderately mobile within the phloem. The isotopic evidence, however, suggests that this flux is not substantial.

Soil texture has considerable influence on the infiltration of sulphur compounds. A sandy texture has a high filtration rate whereas glaciolacustrine clay is much less permeable. This is demonstrated with data from Valleyview, Alberta, by Krouse and Case (1983).

With our increasing sulphur isotope data base, there is evidence that expedient sampling of soil to a preselected depth (usually 5 to 10 cm) may not be a reliable indicator of the pollutant S content. Sulphur in each soil horizon in a core should be examined and the depth profile fully characterized.

Whereas total soil S is most readily analysed to ascertain the penetration of pollutant S into subsoil, specific compounds or compound classes may be more appropriate for study dependent upon the nature of the sulphur source. In the vicinity of industrial SO_2 emitters or sources of S^0 dust, sulphate is the logical choice for two reasons. The added sulphur is initially converted to SO_4^{2-} and the soil sulphate content is usually low (except where gypsum is found in parent material) compared to that of organic S.

In contrast, the penetration of sulphur from manure applications appears to be more readily monitored by analysing the C-bonded S (Chae and Krouse 1986).

4.3.5 Soil Summary Statements

1. Penetration of S-compounds into the soil depends on:
 - a. exposure to emissions;
 - b. continuity of vegetative cover;
 - c. hydrology; and
 - d. parent material.
2. Isotope fractionation among different soil extracts is small except for waterlogged soils where anaerobic SO_4^{2-} reduction may occur.
3. Different S-extracts are more useful than total S for identifying a particular pollutant.
4. Subsurface S-sources may dominate the ecosystem, particularly in depressions.

4.4 VEGETATION

4.4.1 Forms of Sulphur in Vegetation

Plants contain on average about 0.25% S (by dry weight). A wide variety of S-containing compounds have been found in plants, but only a few are known to be required for normal cell function. The essential compounds include the S amino acids, glutathione, thiamine, vitamin B, biotin, ferredoxin, lipoic acid, co-enzyme A, and the sulpholipid of the chloroplasts. A variable but substantial portion of the S in plants is in the form of inorganic SO_4^{2-} .

The largest portion of S in plants is in protein either as cysteine, cystine, or methionine. Plant proteins generally contain 1% S and 17% N (Dijkshoorn et al. 1960; Pumphrey and Moore 1965).

4.4.2 Sulphur Isotope Distribution in Vegetation

Variations in $\delta^{34}\text{S}$ values for vegetation samples from different parts of the world are summarized in Figures 22 and 23. These data, which include many species and parts of individual plants, display a range in $\delta^{34}\text{S}$ values from -39 to $+30$ ‰, similar to those found for sedimentary rocks (Section 2). Whereas parts of some trees were found to vary by less than 1‰, in other cases, variations of over 15‰ were encountered [for Alberta see Krouse et al. (1984) and Legge et al. (1986)].

Extensive studies in the USSR by Chukhrov et al. (1975, 1978) showed that the average and more frequently encountered $\delta^{34}\text{S}$ values are near $+3$ ‰. These authors discussed a number of factors which influence the sulphur isotope composition of vegetation. These include lithospheric sources, groundwater leaching and transport, bacterial redox reactions in soil solutions, and the relative contribution of SO_4^{2-} in precipitation.

Sulphate in the Lena River in the Republic of Central Yakutia, has $\delta^{34}\text{S}$ values as high as $+25$ ‰ due to evaporite dissolution. The $\delta^{34}\text{S}$ values for plants were as high as $+17$ ‰ even at considerable distances from the river. Plants in the flood plain of the Lena River and nearby marshy lowlands possessed higher $\delta^{34}\text{S}$ values. Whereas groundwater played a role in transporting ^{34}S -enriched sulphur to the vegetation, the authors considered local precipitation to be a major factor. They believed that the $\delta^{34}\text{S}$ values ranging from $+5$ to $+22$ ‰ in rain and snow reflected atmospheric uptake from this vast water body.

At some locations, metal sulphide deposits influenced the isotopic composition of plants, whereas in other cases there was no correlation. For example, at Zhosaly Sopka, pyrite deposits contributed negative $\delta^{34}\text{S}$ values to vegetation, whereas at Alaygyur, there was no effect. This was attributed to groundwater circulation and the effects of elevation. Sites below ore deposits could be influenced by leachate carried by groundwater whereas sites above the ore occurrences would not be affected. Negative $\delta^{34}\text{S}$ values in vegetation near copper sulphide occurrences at Kounrad Peaks were in part attributed to ore dust which entered the atmosphere during pit blasting operations.

In some locations, trees growing in igneous rock fissures had foliar $\delta^{34}\text{S}$ values close to the atmospheric average and the seasonal variations were quite small ($+1$ to $+4$ ‰) as compared with the average value of $+2.1$ ‰ found in snow. Precipitation SO_4^{2-} should be rapidly lost through crevices where extensive humic matter had not built up to provide a soil sulphur reservoir. In contrast, large temporal $\delta^{34}\text{S}$ variations were found in locations where plants derived most of their sulphur from soil solutions, particularly under anaerobic conditions. As the consequence of bacterial SO_4^{2-} reduction, the $\delta^{34}\text{S}$ values of residual SO_4^{2-} in stagnant water in a marsh location were found to increase from 0 to 5‰ in the spring to as high as $+29.6$ ‰ in late summer. Birch and willow trees in the same area some distance from the marsh had $\delta^{34}\text{S}$ values near 0‰ whereas grass growing near the stagnant water acquired $\delta^{34}\text{S}$ values as high as $+15.4$ ‰.

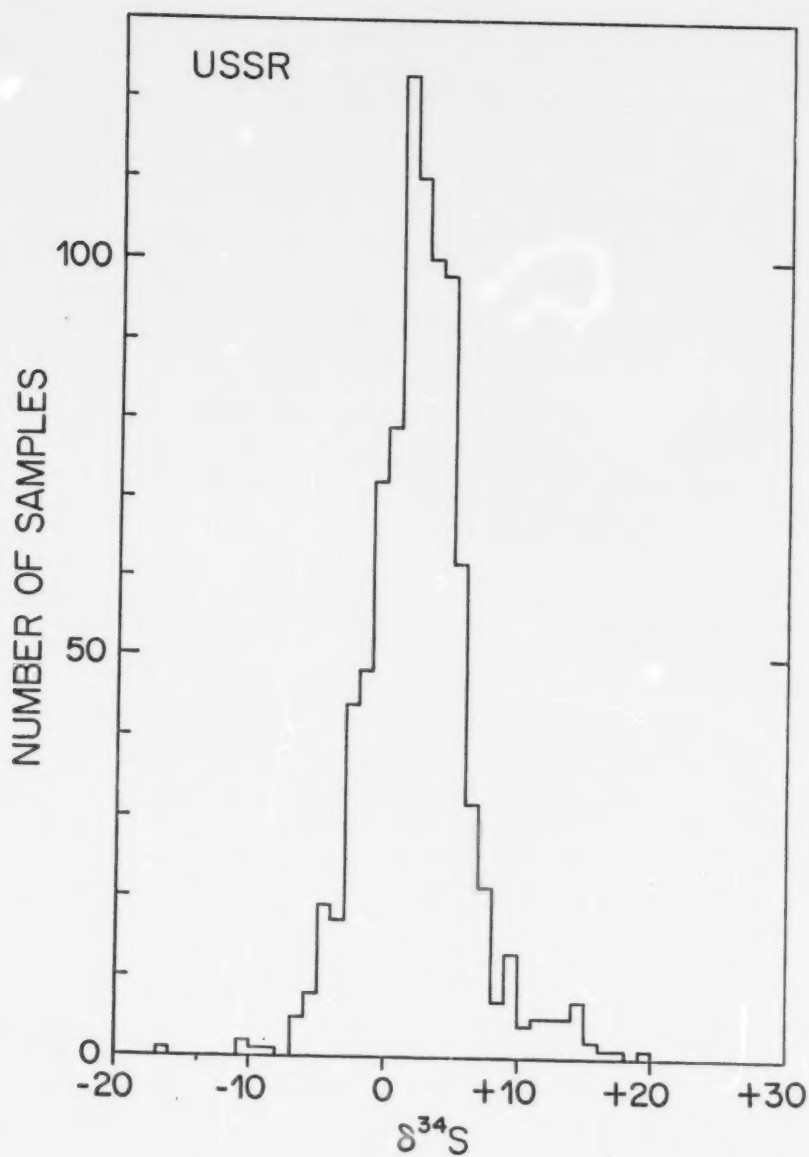


Figure 22. Sulphur isotope data for vegetation in the Soviet Union. Data from Chukhrov et al. (1975, 1978) [see Figure 23]. Figure taken from Krouse et al. (1987).

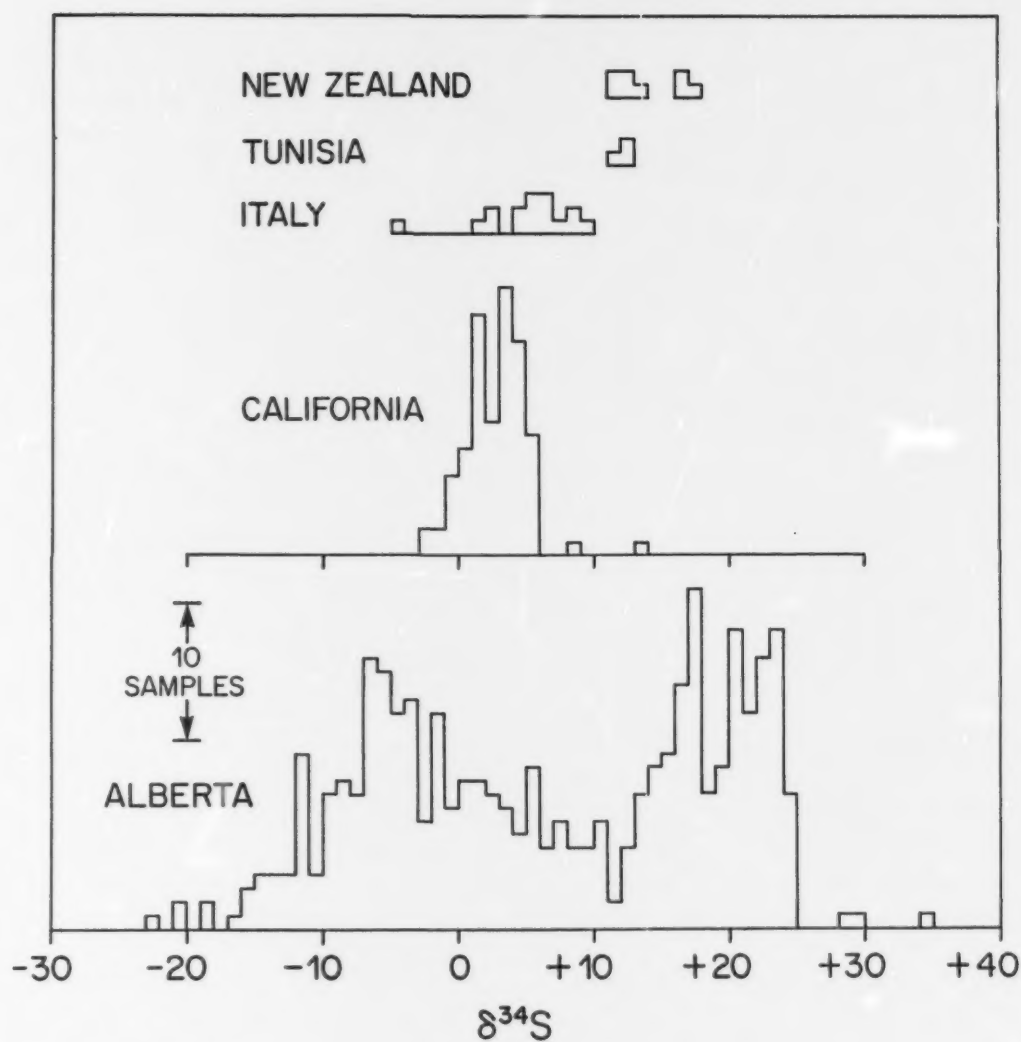


Figure 23. Sulphur isotope data for vegetation throughout the world [see Figure 22]. Figure taken from Krouse et al. (1987).

The data from Alberta contrast with those of the USSR in that they display at least two peaks. The highly negative values are found near Cretaceous shale exposures, particularly in the Peace River area (Krouse and Case 1981). It is believed that they arise from leaching solutions of reduced S species in shales. Occasionally, a highly positive $\delta^{34}\text{S}$ value relates to groundwater leaching of evaporites. However, in most cases, the vegetation is enriched in ^{34}S because foliar S has been derived from atmospheric SO_2 emitted during sour gas processing.

In contrast to the above, limited data from other locations emphasize single sources of soil sulphur. Plants in New Zealand are enriched in ^{34}S in coastal areas because of marine SO_4^{2-} in precipitation (Kusakabe et al. 1976). The positive $\delta^{34}\text{S}$ values for the few specimens from Tunisia relate to gypsum occurrences in the soils (Kusakabe et al. 1976).

4.4.3 Sulphur Isotope Fractionation During Assimilation of Sulphate by Plants and Algae

It is important to know the isotopic fractionation during assimilation of sulphate in order to assess uptake of pollutant sulphur by plants.

Isotope fractionation during SO_4^{2-} assimilation is best measured in the laboratory to avoid problems with multiple sources of sulphur, as discussed below. In the case of algae, the isotopic composition of total sulphur as well as insoluble organic sulphur is typically depleted in ^{34}S by 1 to 2‰ with respect to dissolved sulphate.

With higher plants, either negligible fractionation or depletion of ^{34}S by 1 to 2‰ in the organic sulphur has been realized. In studies with very high SO_4^{2-} or HSO_3^- concentrations, the foliar S may become enriched in ^{34}S due to release of reduced S compounds which are depleted in ^{34}S .

In land plants, the isotopic fractionation during assimilation of SO_4^{2-} in soil water is difficult to evaluate because plants can also acquire sulphur from the air. Therefore, one should examine data from areas where the ambient sulphur oxide concentrations are low compared to the soil SO_4^{2-} content. Further, data for soil solution sulphate should be obtained in the vicinity of the roots.

Examples can be found in the literature where the $\delta^{34}\text{S}$ values for total or organic sulphur in plants are very similar to soluble sulphate in the soil. Mekhtiyeva et al. (1976) studied six perennial plants near Moscow during the growing season. The total foliar sulphur was slightly depleted in ^{34}S with respect to soil sulphate. There were temporal trends with the conifers becoming more depleted and the deciduous trees (linden, poplar, birch, and elm-leaved spirea) becoming more enriched in ^{34}S during the period May to September. This suggests that gymnosperms respond differently than angiosperms.

Isotopic similarity of foliar sulphur and soil solution sulphate is usually found where soils are high in S content, and uptake of atmospheric S by the plant is comparatively minor. Included are soils enriched in ^{34}S because of dissolution of evaporites or sea spray fallout in coastal regions (Figure 24). Alternatively, if the sulphur is derived almost entirely from precipitation, the $\delta^{34}\text{S}$ values of the foliar sulphur are also nearly the same as the dissolved sulphate. This was found where plants grew in granitic rock fissures (Chukhrov et al. 1975).

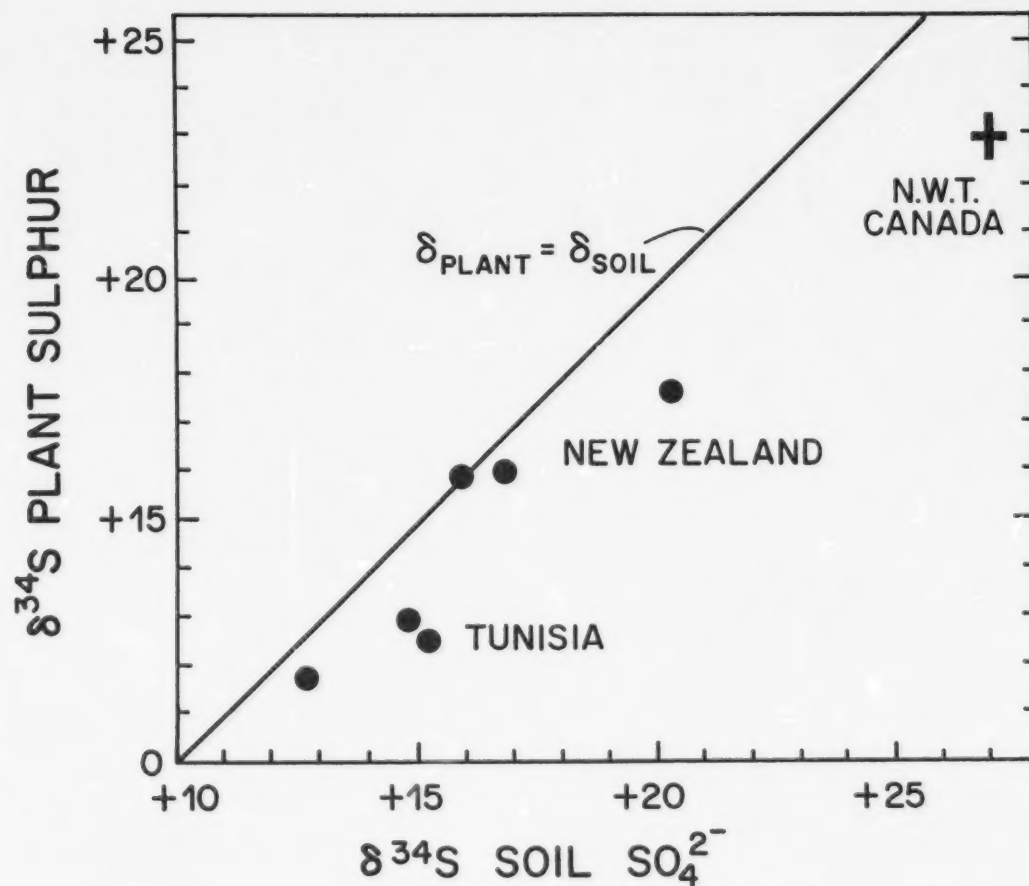


Figure 24. $\delta^{34}\text{S}$ values of total S in plants versus that of soluble S in associated soil. Individual data points for New Zealand and Tunisia from Kusakabe et al. (1976). The NWT data represent several samples from one location. Figure taken from Krouse et al. (1987).

Another approach to evaluating isotopic fractionation during SO_4^{2-} assimilation is to compare the $\delta^{34}\text{S}$ value of water-soluble foliar S to the total or insoluble S. Data for specimens from various parts of Japan are found in Figure 25. It is noted that many points fall close to the line of unity slope going through the origin. There is a slight tendency for points to plot above the line suggesting that on average, foliar organic sulphur is 1 to 2‰ lighter than the soluble S.

It would appear that in situations where ambient SO_2 is low and uptake of soil sulphate is the main mechanism, the soluble and insoluble sulphur have similar sulphur isotope compositions. If the uptake of atmospheric sulphur compounds is pronounced, then different extracts and indeed different parts of a plant may differ markedly in isotopic composition. It is interesting to note that the soluble S component is more mobile and should generally be more recent than the organic S pool. Hence, deviations from the line of unity slope in Figure 25 could reflect temporal changes in the isotopic composition of the source SO_4^{2-} . Such comparisons can potentially serve to monitor changes in pollutants present in the soil or atmosphere.

In summary, as with aquatic plants and bacteria, sulphur isotope selectivity during SO_4^{2-} assimilation by land plants is small, with a tendency for the organic S to be relatively depleted in ^{34}S by 1 to 2‰.

There is also evidence that when atmospheric SO_2 is absorbed by lichens, the transformation to organic sulphur involves very little isotopic selectivity (Krouse 1977b).

4.4.4 Uptake of Sulphide by Plants and Algae

There is growing evidence that certain aquatic plants are able to utilize dissolved sulphide species. Fry et al. (1982) found submerged and merged rooted plants in anoxic sediments to have $\delta^{34}\text{S}$ values near that of the sulphide species (-24‰) rather than the SO_4^{2-} in the interstitial porewater (+15 to +17‰). They could not ascertain whether sulphide was incorporated directly or whether it was oxidized at the root-sediment interface. Carlson and Forrest (1982) found the salt marsh cordgrass, *Spartina alterniflora* to be isotopically similar to sulphide in the marsh porewater. They concluded that sulphide had been oxidized within the plant.

Sulphur in algae is generally slightly depleted in ^{34}S with respect to seawater sulphate. Lacking roots, algae do not have access to sulphide in the sediments. These observations are in contrast to studies with algae in thermal springs (Krouse et al. 1970; H.R. Krouse and A. Sasaki, unpublished data). If HS^- is present, the algae tend to reflect the isotopic abundance of the HS^- rather than that of SO_4^{2-} which may be two or three orders of magnitude more abundant. Sulphate crystallization was found in the midst of some algal mats and its $\delta^{34}\text{S}$ value was similar to the dissolved sulphide species. The sulphur oxidizing bacteria *Beggiatoa* sp. were also found associated with some algae (F.D. Cook, private communication).

4.4.5 Relative Uptake of Atmospheric and Soil Sulphur Compounds by Vegetation

Most vegetation can acquire sulphur from the atmosphere or from sulphate solutions either in soil or water bodies. Uptake from these two reservoirs can be readily verified if their sulphur isotopic compositions differ (Krouse 1977b).

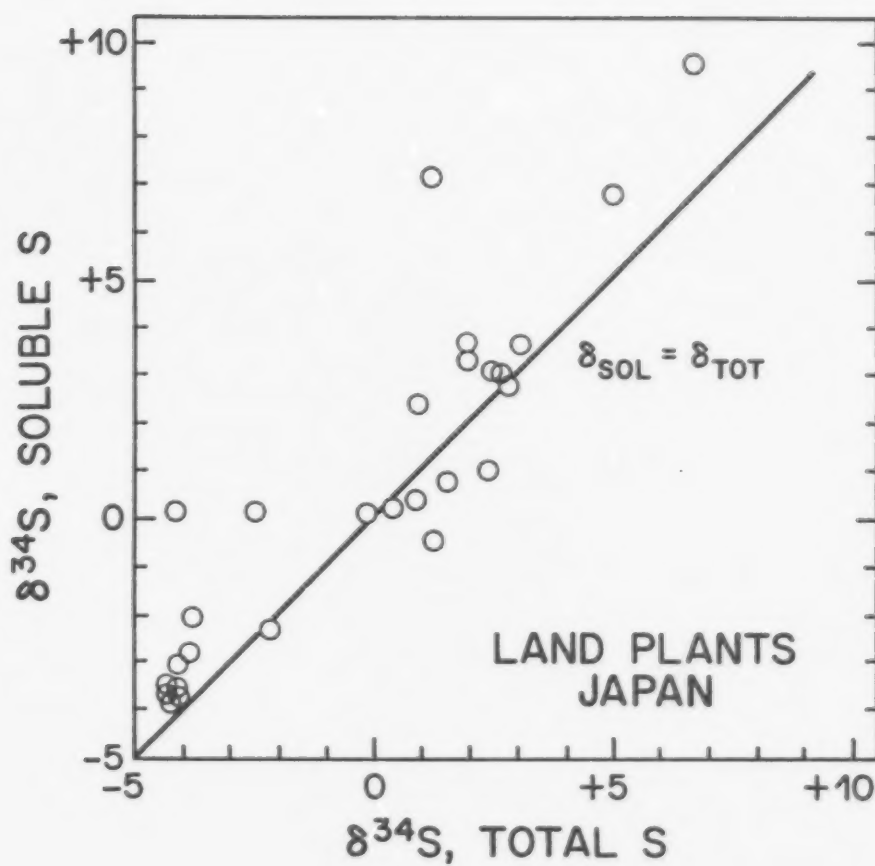


Figure 25. $\delta^{34}\text{S}$ values of soluble S versus that of total S in plants in Japan. Data supplied by N. Nakai. Figure taken from Krouse et al. (1987).

In some situations one uptake mechanism dominates. As shown by Winner et al. (1978) epiphytic lichens in the Fox Creek area of Alberta have $\delta^{34}\text{S}$ values close to that of ambient SO_2 unless under severe stress. This indicates direct uptake of atmospheric SO_2 or contact with SO_4^{2-} which has formed by SO_2 oxidation.

Another example of a dominant uptake mechanism is the acquisition of sulphur dust by bark as shown by Legge et al. (1986) working in the Whitecourt area. Some of the dust can be oxidized, and the sulphate in turn converted to insoluble organic S. However, large quantities of elemental S can also be entrapped by the bark.

Conifer needles and deciduous leaves have $\delta^{34}\text{S}$ values intermediate to the air and soil, indicative of uptake from both sources. The extent to which sulphur is derived from either source depends upon a number of factors such as the relative concentration of available sulphur and the physiological response of the plant. Although high concentrations of SO_2 may damage higher plants, there is also evidence that atmospheric sulphur compounds can provide nutritional needs (Faller et al. 1970; Cowling et al. 1973). The concentration at which SO_2 exposure is injurious is not well defined and is species specific. It depends upon factors such as duration and intensity of exposure, susceptibility of the species, stage of growth, humidity, soil moisture, and light intensity. On the basis of experiments of Zahn (1961), 0.15 ppm ($420 \mu\text{g SO}_2 \text{ m}^{-3}$) is gaining acceptance as a threshold below which prolonged exposure will not be detrimental.

The two uptake pathways are also expressed in the isotopic variability among different parts of an individual plant. In the studies of Chukhrov et al. (1975, 1978), plant parts were found to be uniform in isotopic composition. In other studies, considerable variability has been found. These variations can be explained by the results of potted plant experiments conducted by Winner et al. (1978). Plants grown in the laboratory and the associated soil had $\delta^{34}\text{S}$ values near -8‰ . In early June, they were exposed to ambient SO_2 with $\delta^{34}\text{S}$ values near $+20\text{‰}$. The $\delta^{34}\text{S}$ values of the plants and soil were found to increase uniformly throughout the growing season if the soil surface was exposed. If charcoal, peat, or moss were placed on the surface, the soil tended to retain the $\delta^{34}\text{S}$ value established in the laboratory. The foliage of plants grown in covered soils did not increase in $\delta^{34}\text{S}$ values as quickly as those in uncovered soils because pollutant S was acquired only from the atmosphere. In the exposed surface case, sulphur of industrial origin was acquired by the plants from both the atmosphere and soil.

The potted plant experiments imply that in the environments examined by Chukhrov et al. (1975, 1978), either the uptake of atmospheric S compounds by foliage was minimal or the soil and air had similar isotopic compositions.

The relative rates of uptake of sulphur from the soil and atmosphere may also be manifested in the height dependence of the isotopic composition of foliage. Whereas foliage near the top in a stand of trees tends to interact with sulphurous compounds in the atmosphere, lower foliage may take up its sulphur almost entirely from the soil. This is a consequence of the upper foliage exerting a canopy action on the lower branches (Lester et al. 1986). This has been noted on many occasions in forest ecosystems exposed to emissions from the sour gas industry in Alberta but is best documented for the Whitecourt area (see Legge et al. 1978; and Legge et al. 1986). This variation with

height becomes more pronounced if the vegetation emits H_2S under high sulphur stress (Krouse et al. 1984).

The relative rates of acquiring sulphur from the atmosphere and soil can also be noted in the examination of different species. If industrial emissions are minimal, $\delta^{34}\text{S}$ values for both lichens and pine needles tend towards a similar $\delta^{34}\text{S}$ value at higher natural concentrations. If the isotopic composition of the air differs from that of soil because of industrial emissions, the $\delta^{34}\text{S}$ values of lichens reflect the atmosphere, whereas the needles isotopically reflect both sources. If industrial emissions dominate the environment for a few years, the $\delta^{34}\text{S}$ values for lichens and needles acquire the industrial isotopic signature.

There are topographical factors which indirectly influence the amounts of sulphur acquired by the plants from soil and air (Figure 26). High foliar sulphur concentrations may not be consistent with the $\delta^{34}\text{S}$ values identified with the industrial emissions. Through sub-surface leaching, salts high in sulphate may accumulate in depressions. Trees growing in this environment would have a high foliar S content and a small addition of industrial S could prove quite harmful. However, the needles would retain a $\delta^{34}\text{S}$ value close to that of the soil sulphate and not distinguish the relatively minor industrial admixture. In contrast, a nearby tree on an exposed knoll may be growing in sulphur-deficient soil and additions of the atmospheric pollutant sulphur could prove beneficial. This healthy foliage could have a lower sulphur content than that of the stressed foliage in depressions, but have $\delta^{34}\text{S}$ values near that of the industrial emissions.

4.4.6 Relationships Between $\delta^{34}\text{S}$ Values and Biological Parameters

Sulphur isotope abundances readily establish the presence of pollutant sulphur in the environment. The problem of relating anthropogenic sulphur to environmental damage is far more difficult and requires relating ecological parameters to the isotope data.

One biological criterion is ground coverage of species, particularly those which are very sensitive to the pollutant of interest. Data from the Fox Creek area show that for both an angular and distance traverse with respect to the dominantly downwind direction, reduction in coverage of mosses corresponds to larger proportions of sulphur of industrial origin in the vegetation (Figure 27).

A biological damage indicator can often be related to sulphur isotope composition and hence the presence of pollutant sulphur. However, this coincidence is not proof that damage was due to the anthropogenic sulphur. Other pollutants may be detrimental. There may also be secondary effects such as lowering of the Se:S ratio or undesirable chemical reactions (e.g., dissolution of metals or acidification).

4.4.7 Emission of Reduced Sulphur Compounds by Vegetation

Plants under high sulphur stress have been shown to emit H_2S (Decormis 1968; Spaleny 1977; and Wilson et al. 1978). These emissions are enhanced by light and other factors such as the extent of root damage. In laboratory experiments with cucumber plants, the emitted H_2S was found to be significantly depleted in ^{34}S in comparison with SO_4^{2-} and HSO_3^- solutions surrounding the roots (Winner et al. 1981).

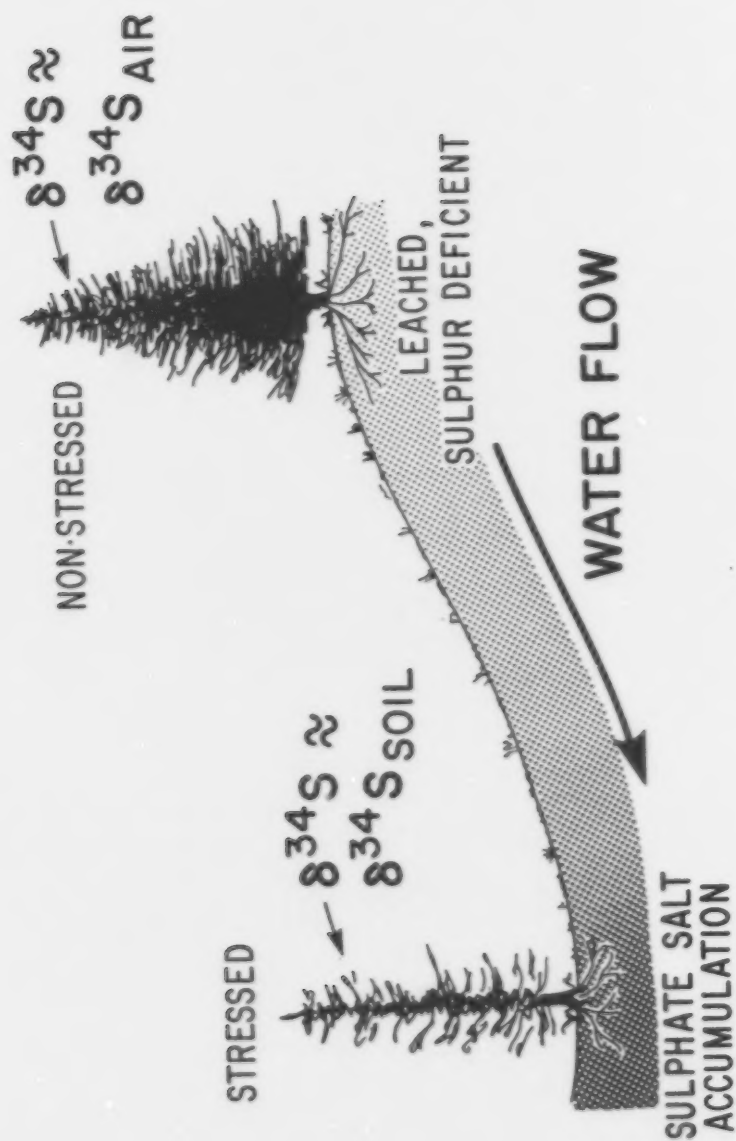


Figure 26. Possible influence of topography on the sulphur isotope composition of vegetation. Because of subsurface leaching and transport, plants in depressions may be S-stressed and display a natural isotopic signature. Plants on knolls may grow in S-deficient soil but acquire much of their nutrient S from the atmosphere (taken from Krouse et al. 1987).

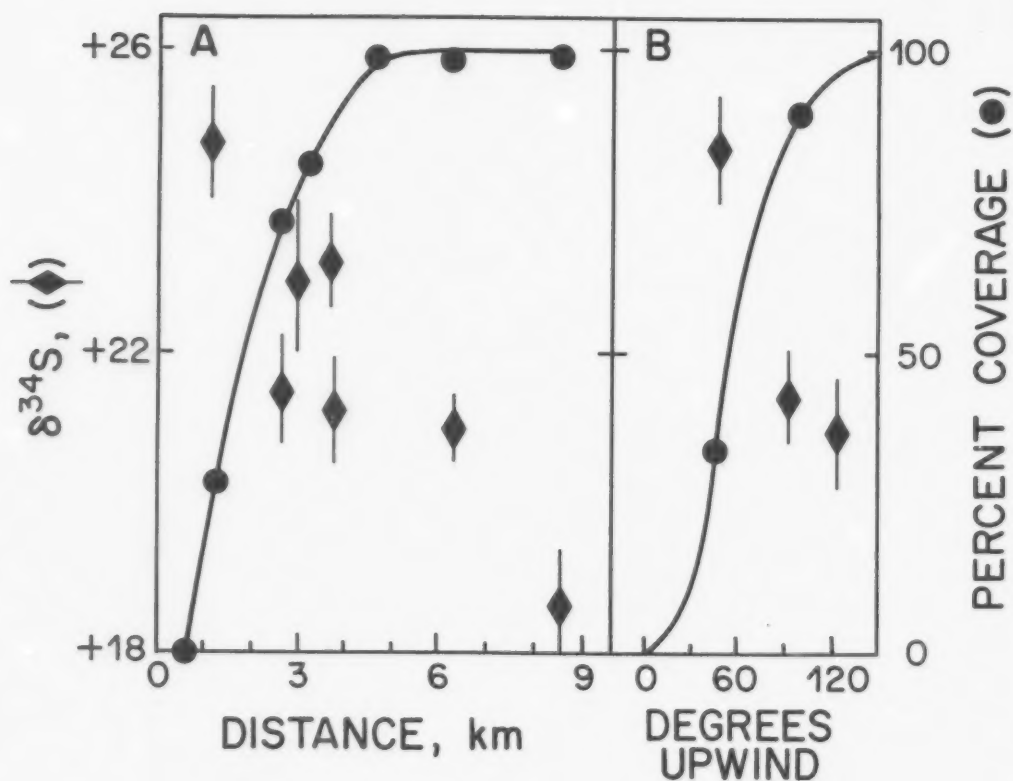


Figure 27. Relationship between $\delta^{34}\text{S}$ values and ground coverage of mosses near a sour gas processing plant at Fox Creek, Alberta for a distance (A) and an angular (B) traverse with respect to the downwind direction. Vertical bars represent the standard deviation about the mean (from Winner et al. 1978, in Krouse et al. 1987).

Sulphur isotope data provide indirect evidence that such gaseous emissions occur in nature. In areas of high S stress, foliar S has $\delta^{34}\text{S}$ values which are considerably higher than any available S sources. This is illustrated with data on lichens near Fox Creek and lodgepole x jack pine needles in the West Whitecourt Study region (Case and Krouse 1980; Krouse et al. 1984).

Further evidence is suggested by the isotopic composition of salt crystals which occur occasionally on plant leaves. Two situations were examined by Shakur (1982). Evaporite crystals on vegetation near Kelly Lake Springs ($65^{\circ}24'\text{N}$, $126^{\circ}06'\text{W}$) were found to have $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values very similar to those for SO_4^{2-} in the spring waters. In these springs, the $[\text{SO}_4^{2-}]$ ranged from 250 to 800 ppm. This contrasts markedly with an unusual natro-jarosite, $\text{NaFe}_3(\text{OH})_6(\text{SO}_4)_2$, depositing spring ($65^{\circ}12'\text{N}$, $124^{\circ}38'\text{W}$) near Norman Wells, NWT. In these waters, the $[\text{SO}_4^{2-}]$ is much higher, at 5300 ppm. The $\delta^{34}\text{S}$ values of the mineral deposits are very close to that of SO_4^{2-} in the spring. Crystals of various sulphates occur on vegetation around this spring. In contrast to the brilliant yellowish-orange colour of the jarosite, these crystals are white and do not contain iron. They are also enriched in ^{34}S by over 3‰, as compared to the spring SO_4^{2-} and mineral deposit. In this depositional environment where H_2S evolution is absent, this enrichment is judged to be significant.

Thus, in areas of high S stress $\delta^{34}\text{S}$ values have been found for lichens, needles, and salt crystals on vegetation, which are higher than for any source of sulphur in the vicinity. This implies a loss of ^{34}S -depleted sulphur from the vegetation. Such a loss is consistent with a reductive process in which the ^{32}S species react at a faster rate.

Arguing conversely, $\delta^{34}\text{S}$ values in vegetation that are more positive than the available sulphur nutrients could be indicative of high sulphur stress.

4.4.8 Vegetation Summary Statements

1. Epiphytic lichens derive S mainly from the atmosphere.
2. Rooted plants can derive S from the soil and the atmosphere.
3. Foliage under S-stress emits gaseous reduced S-compounds. This process is isotopically selective.
4. Upper foliage in a canopy may shield lower foliage from atmospheric S-compounds.
5. In rolling terrain, the S-content of foliage can vary significantly with elevation because of subsurface dissolution and precipitation of sulphate salts.

4.5 HIGHER MEMBERS OF FOOD WEBS

Higher members of food webs lack the ability to convert inorganic sulphate to amino acids such as cysteine and methionine (assimilation), and must ingest essential organo-sulphur compounds. Isotopic selectivity during assimilation by aqueous plants and animals tends to be small. Similarly, assimilation of sulphate by terrestrial plants appears to be accompanied by minimal isotopic fractionation (Section 4.4.3).

Whereas higher members of food webs lack the sulphate assimilation capability, biochemical pathways are available for interconversions of sulphur amino acids. Because these pathways involve large molecules, accompanying isotopic selectivity is expected to be small. Indeed, it would appear that the fractionation becomes smaller with progression up a food chain.

Sulphur isotope fractionation in a food chain can be best evaluated where one source of sulphur dominates, such as marine sulphate with a $\delta^{34}\text{S}$ value near $+21\text{‰}$. Shifts to lower $\delta^{34}\text{S}$ values by as much as 3‰ are found for marine algae and plants. Salmon off the coast of western Canada have $\delta^{34}\text{S}$ values of $+18$ to $+19$ for inner flesh and $+20\text{‰}$ for the skin. In the Canadian Arctic, the fur of polar bears tends to have values near $+17\text{‰}$ as compared with values between $+16$ and $+18\text{‰}$ for the fur of seals, their main food source. Thus, sulphur of marine origin has progressively moved up this food chain.

Heron Island on the Great Barrier Reef of Australia has a large bird population because of the absence of predators. The combination of sea spray sulphate and fertilization by birds that are primarily fish feeders has resulted in the soil, vegetation, and feathers of birds having a remarkably uniform $\delta^{34}\text{S}$ value near $+19\text{‰}$.

The fur of koala bears is about 2‰ depleted in ^{34}S as compared with the eucalyptus leaves they consume. The hair of kangaroos was found to have a sulphur isotope composition close to the mean of their known food sources (Figure 28).

Sulphur isotopic compositions have been determined for hair, nails, blood, urine, and cystine kidney stones in humans. The overall variation in $\delta^{34}\text{S}$ of these components in a given human is about 2‰ and appears to approximate the mean sulphur isotope composition of the diet. Data are shown for residents of Calgary, Alberta, Canada in Figure 29. The $\delta^{34}\text{S}$ values for available foods range from near $+20\text{‰}$ down to -7‰ . The positive extreme corresponds to imported seafood whereas the most negative value corresponds to cereals processed in eastern Canada. Local beef and pork as well as dairy products which constitute a large part of the diet tend to be close to 0‰ . It is seen that hair, nails, blood, urine, and cystine kidney stones in Calgary residents are also close to 0‰ . There was no discernable difference in the sulphur isotope composition of kidney stone formers and non-formers.

In contrast to the narrow range of isotopic composition within one individual, large variations have been found in the isotopic composition of hair, nails, and kidney stones with geographical location (Krouse and Levinson 1984; A. Sasaki, unpublished data). For example, the $\delta^{34}\text{S}$ values for nails of attendees at the 1983 SCOPE/UNEP Sulphur Workshop in Pushchino, USSR, ranged from $+3$ to $+14\text{‰}$.

From the above, it follows that if a human increases the marine food content of his diet, the $\delta^{34}\text{S}$ value of his tissues and fluids increase. $\delta^{34}\text{S}$ values for whiskers of a Calgarian ranging between $+1.5$ and $+2.0\text{‰}$ increased to $+3.1\text{‰}$ after the individual resided for one month in Japan. Upon returning to Calgary, the values returned after about six weeks to the pre-visit levels (Table 2).

The oxygen isotope data for SO_4^{2-} in urine from the above study are also interesting (Table 2). They reflect the greater ^{18}O depletion in drinking water of Calgarians in comparison to Japanese and imply that some oxygen from body water molecules is incorporated into SO_4^{2-} during biochemical oxidation.

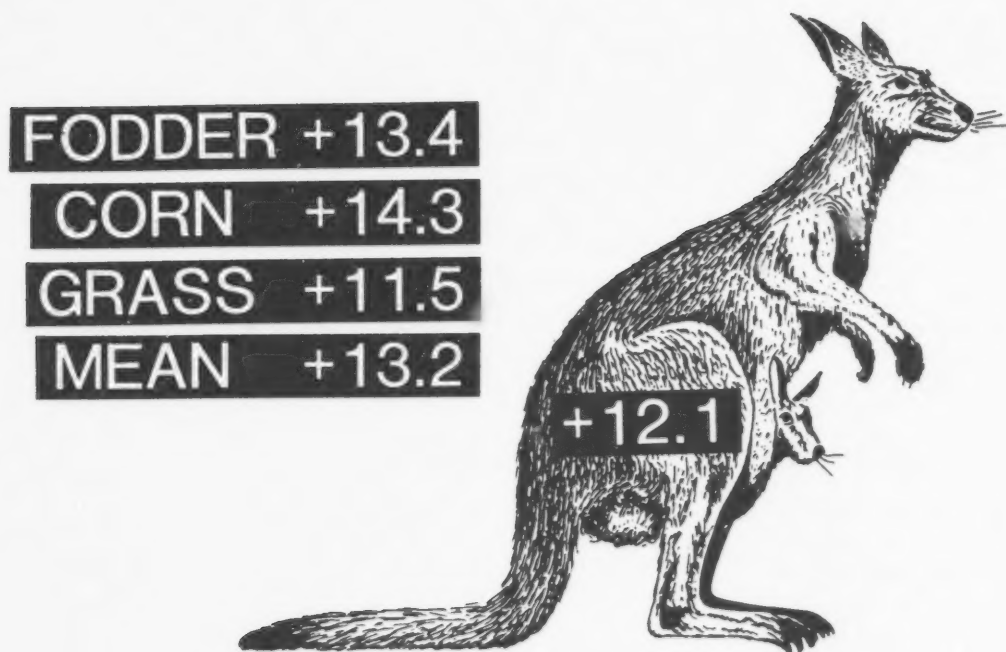


Figure 28. $\delta^{34}\text{S}$ value of hair of kangaroos in comparison to that of their diet.

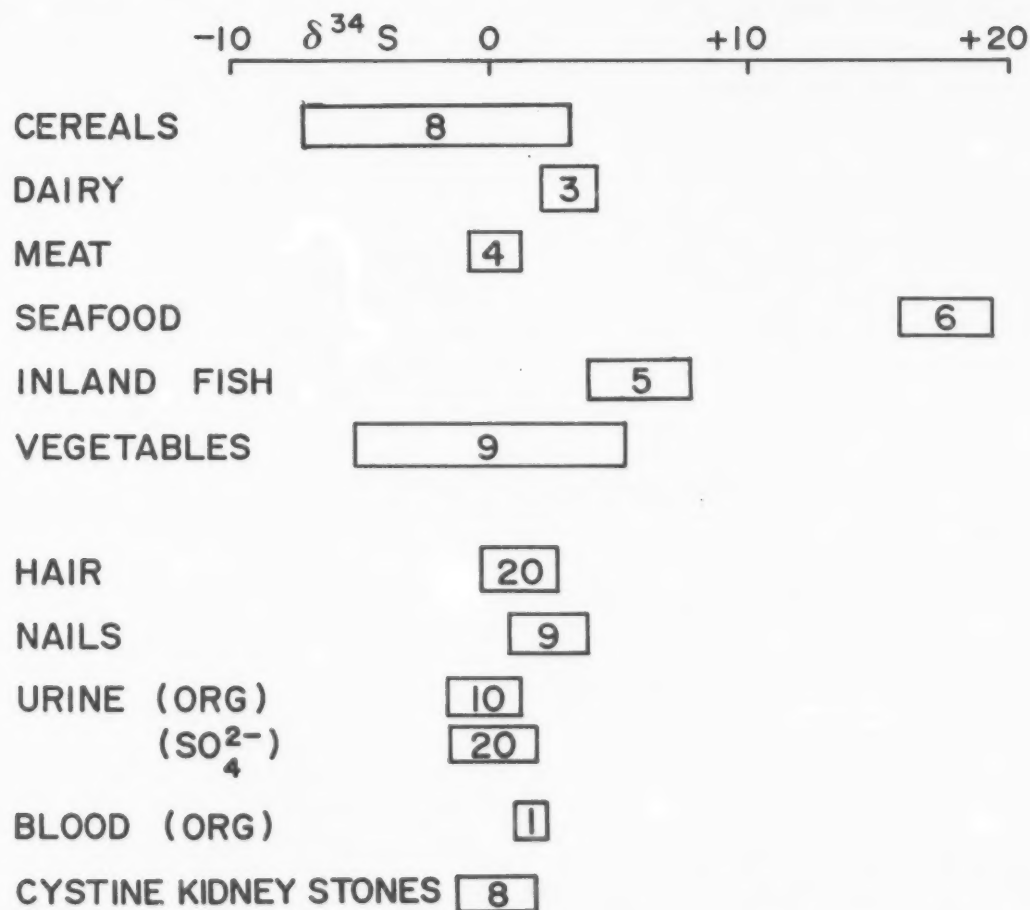


Figure 29. $\delta^{34}\text{S}$ values of human body components of Calgarians compared to potential foods. The numbers in the boxes correspond to the number of specimens.

Table 2. Changes in sulphur isotope composition of Calgarian who visited Japan for one month.

Sample Time	$\delta^{34}\text{S}$		$\delta^{18}\text{O}$ (SMOW)
	Whiskers	Urine SO_4^{2-}	Urine SO_4^{2-}
Pre-Visit	+1.5 to +2.0	-0.1	-5.8
End of Visit	+3.1	+2.1	-2.3
Back in Calgary			
3 days		+1.5	-3.0
7 days	+2.4	+0.6	-3.7
14 days		+0.4	-4.2
28 days	+2.0	+0.2	-5.8
35 days	+2.0		

The ability to incorporate reduced sulphur compounds appears not to be limited to certain plants and algae (Section 4.4.4). Dense animal assemblages near deep sea hydrothermal vents, including vestimentiferan worms, brachyuran crabs, and giant clams were found to have $\delta^{34}\text{S}$ values near $0^\circ/\text{‰}$, close to the range for nearby sulphide minerals (Fry et al. 1983). It seems unlikely that the vent fauna utilized sulphide directly. Primary productivity was probably due to chemoautotrophic bacteria utilizing sulphide as an energy source. In some instances, sulphur oxidizing bacteria may have functioned symbiotically within tissues of host animals.

A comprehensive isotopic study has not been carried out to date on the extent that sulphur originating from industrial processing can be found in higher members of the food web. The feathers of grouse living downwind of a sour gas plant in Alberta, Canada were found to have $\delta^{34}\text{S}$ values near $+10^\circ/\text{‰}$, whereas specimens from a non-industrial location were near $0^\circ/\text{‰}$. This suggests that about one half of the sulphur in the former can be attributed to industrial sulphur ($\delta^{34}\text{S} = +22^\circ/\text{‰}$) incorporated in vegetation consumed by the bird.

Environmental studies with widely ranging foragers have logistic advantages. For example, the isotopic composition of one bee should represent the average for thousands of plants in an area. It must be emphasized that such studies are potentially useful for only long-term phenomena. A short-term exposure to small amounts of H_2S which may be lethal would not be revealed by isotopic analyses because of the large reservoir of biological sulphur present in the animal. Further, unlike plants and soil, one should not expect to observe radical variations in sulphur concentration. For example, the sulphur content of hair is about 4 percent as dictated by its molecular composition.

Studies of possibly related phenomena may be feasible. The extent to which the Se/S ratio is depressed in the environment by industrial sulphur additions should be discernable by plotting this ratio against the sulphur isotopic composition. The isotopic compositions of metals, with the exception of lead, are difficult to determine. However, if metals arise from a process where sulphur emissions are involved, such as ore roasting, then plots of metal concentrations versus $\delta^{34}\text{S}$ values may prove informative.

The use of stable isotopes of several elements can prove very useful for complex food web analyses. A combination of stable isotopes of sulphur, carbon, and nitrogen were found to eliminate many ambiguities in tracing organic matter flow in salt marshes and estuaries (Peterson et al. 1985).

5. CONCEPTUAL MODELLING OF SULPHUR ISOTOPE ABUNDANCES IN THE ENVIRONMENT SURROUNDING SOUR GAS PLANT OPERATIONS

Sulphur isotope data for soil and foliage from many locations in Alberta can be synthesized into a composite diagram (Figure 30). In areas which have not been influenced by industrial sulphur emissions, the natural $\delta^{34}\text{S}$ values are near 0‰ or negative. The $\delta^{34}\text{S}$ values of the soil versus those of the corresponding foliage fall on the line of unity slope. This reflects leaves deriving the bulk of their sulphur from the soil during growth, and returning sulphur to the soil upon decay. In the intermediate situation where there is some fallout of industrial sulphur enriched in ^{34}S , the soil tends to be isotopically lighter than atmospheric sulphur compounds for two reasons. The leaves contain isotopic mixtures of sulphur derived from the soil and air, and organic cover may limit the penetration of atmospheric compounds into mineral soil horizons. Therefore, data plot above the line of unity slope (Figure 30).

In industrial areas where sulphur compounds have penetrated the soil, the atmosphere, soil, and foliage have similar but higher $\delta^{34}\text{S}$ values because of the prevalence of sulphur of industrial origin. Therefore, points also fall on the line of unity slope.

In preliminary studies in the Ram River area, it was concluded that epiphytic lichens acquired a sulphur isotopic composition similar to that of the atmosphere (Krouse 1977). This relationship does not hold true for all types of lichens and mosses. In particular, species dwelling near the ground appear to acquire some sulphur from the litter layer and may have $\delta^{34}\text{S}$ values intermediate to the epiphytic lichens and leaves. The leaves in turn have isotopic compositions consistent with a mixture of sulphur derived from the atmosphere and soil. These observations suggest another synthesis of isotopic data in which vegetation is further subclassified by elevation (Figure 31).

In this conceptual model, it is postulated that $\delta^{34}\text{S}$ values progressively increase, going from the deep soil horizons upwards to epiphytic lichens in response to industrial sulphur deposition. It is assumed that the pre-industrial $\delta^{34}\text{S}$ value of the environment was zero or lower and that all soil layers and vegetation had similar values.

The "intermediate" pattern can arise when the levels of sulphur of industrial origin in environmental samples are comparable to those of background sulphur. This situation should not be considered in terms of absolute sulphur content. For example, if the natural sulphur content were low, the environment could remain depleted in sulphur even with industrial contributions and would display the intermediate pattern.

In the intermediate situation, it is expected that some of the ^{34}S enriched industrial sulphur compounds will have penetrated the soil. The concentrations of these compounds and their $\delta^{34}\text{S}$ values tend to decrease with depth. The $\delta^{34}\text{S}$ value for atmospheric compounds will be slightly less than that of the industrial emitter because of dispersion and mixing with background sulphur sources. Epiphytic lichens tend to isotopically resemble the atmosphere. Trees tend to be isotopically intermediate to soil and atmosphere. Trees may display a height trend with upper needles or leaves more enriched in ^{34}S than lower ones. This is attributed to the upper foliage acquiring proportionally more atmospheric S and exerting a canopy action on the lower foliage (Krouse et al. 1984).

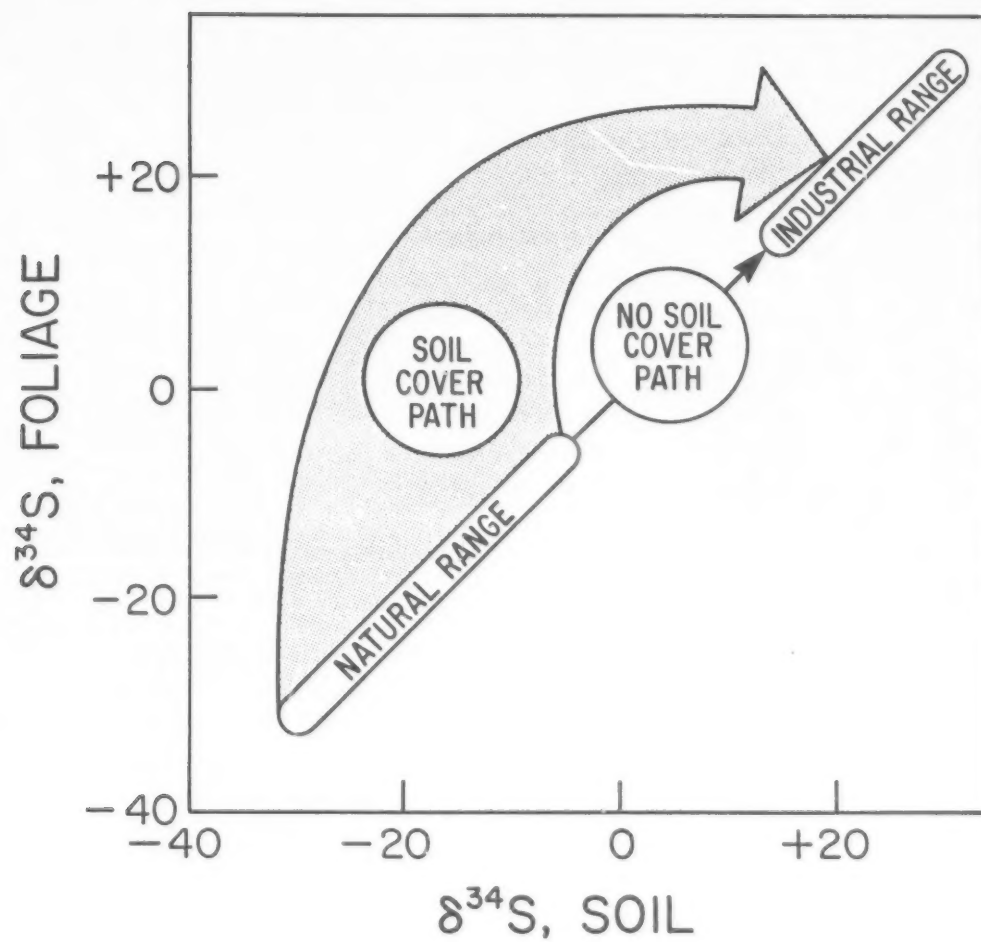


Figure 30. Relationship between vegetation and soil sulphur isotope composition in response to emissions from sour gas processing.

In the high industrial input situation, the isotopic composition for all components is essentially that of the emissions. This does not necessarily imply that the sulphur content of the environment is excessive but rather that the majority of measured sulphur is of industrial origin.

If excessive sulphur is present, $\delta^{34}\text{S}$ values for epiphytic lichens and pine needles may be much higher than that of ambient SO_2 (Case and Krouse 1980; Krouse et al. 1984). This is attributed to isotopically selective emission of sulphur compounds by vegetation under sulphur stress (Winner et al. 1981).

6. RECOMMENDATIONS FOR FURTHER RESEARCH

Whereas more sulphur isotope data have been acquired for the environment in Alberta than elsewhere in the world, this situation will not remain for long. It is clear that other regions will soon have comparable data bases. In the case of Alberta there remain a number of areas where more data and testing of concepts are desirable.

6.1 NON-UNIFORMITY OF DATA COVERAGE FOR GAS PLANTS

Data acquisition has been biased in terms of sites surrounding a few sour gas plant installations rather than a methodical provincial survey. There are regional gaps where sour gas plants are active, but isotope data have either not been acquired or are not in the public domain. For other gas plants, there were only a few measurements taken at one point in time.

In the meantime, operating conditions may have changed. In some cases, gaseous emissions were reduced but sulphur dust release has increased. Therefore, spatial and temporal data gaps in the Provincial data base should be addressed.

6.2 OTHER SOURCES OF SULPHUROUS EMISSIONS

Data have not been acquired for other industrial emitters of sulphur compounds in the Province. For example, most of the coal in Alberta has a sulphur content well below one percent, but large amounts are combusted in power stations. For completeness, a provincial environmental sulphur isotope base should include studies of such emitters.

6.3 OXYGEN ISOTOPE COMPOSITION OF SULPHATE

Oxygen isotope data for sulphate in wet- and dryfall in Alberta are virtually non-existent. As discussed in Section 3, the extent to which the oxygen isotope composition of SO_4^{2-} correlates to that of the associated water is a measure of the involvement of that water in the oxidation of reduced S-compounds. Once SO_4^{2-} is formed, its oxygen isotope composition is preserved under most environmental conditions. Therefore, oxygen isotope data for SO_4^{2-} can potentially delineate SO_4^{2-} formed in stacks, SO_4^{2-} formed by oxidation of SO_2 in the atmosphere, long range transported SO_4^{2-} , and SO_4^{2-} formed by oxidation of S^0 . An extended precipitation study over many years is merited. Field experiments should be set up to investigate SO_4^{2-} produced during oxidation of S^0 in soil or entrapped in bark.

6.4 LAKE SEDIMENTS

Because isotope data were not acquired prior to the start-up of most sour gas processing plants, environmental receptors with a progressive (rather than accumulative) record of sulphur uptake should be examined. Tree rings have been used successfully with other elements but, unfortunately, the S-contents are low. Glacier cores are another possibility but again the SO_4^{2-} concentrations are extremely low. However, studies of lake sediments over small depth increments have proved to be informative in the Great Lakes region and upper New York State. Similar studies should be conducted on lakes in Alberta to see if a time-marker is registered by an isotopic signature attributable to industrial processing. Coincidentally, this would provide information on just how well the lakes have coped with inputs of sulphur from precipitation and runoff.

6.5 HIGHER MEMBERS OF THE FOOD CHAIN

As sulphur is passed up the food chain, the isotopic selectivity is minimal. Data have only been acquired for humans in one urban environment in Alberta. A few isolated measurements have been carried out with insects and hair of animals. More data should be acquired for insects, small mammals, and fish to document migration of sulphur of industrial origin up food chains in Alberta.

6.6 DATA BASE

In order that isotopic data can be better related to region, surface geology, natural and anthropogenic emissions, and so forth, an active computer data base should be established.

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